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(54) TITANIUM ALLOY AND METHOD OF MANUFACTURING A TITANIUM ALLOY

(57) According to an aspect of the disclosure an ($\alpha+\beta$)-titanium alloy consists of, in % in weight: Al: 3.0 to 7.0%, (Fe + Cr + Mn): 1.5 to 4.5%, with Cr less than Fe, Mn less than Fe, and Cr less than 1.5%, (Sn + Zr): 1.0 to 5.0%, with Zr less than 0.8%, O: 0.03 to 0.35%, and optionally one or more of (V + Mo + Nb + Ta): less than 3.0%, B: less than 1.0%, C: less than 0.08%, N: less than 0.05%, H: less than 0.015%, the balance Ti and incidental impurities.

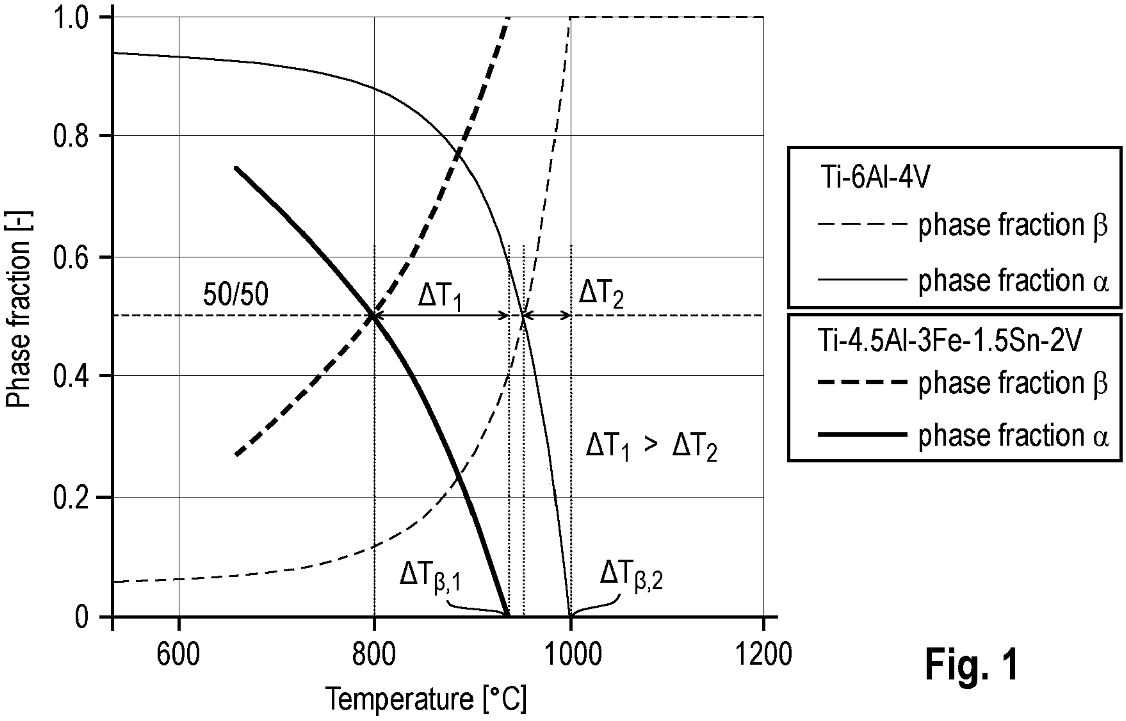


Fig. 1

Description

Technical Field

[0001] This disclosure relates to titanium alloys, and in particular to an (α+β)-titanium alloy with high ballistic performance and/or applicability in medical technology or aerospace applications.

Background

[0002] Ti-6Al-4V (Grade 5) is the most widely used (α+β)-titanium alloy with a market share of more than 50%. (α+β)-titanium alloys such as Grade 5 are suitable for applications in the high-performance sector due to their balanced mechanical properties and low density.

[0003] Despite the wide range of applications, Grade 5 is not optimized for applications in the defense sector and, in particular, with regard to ballistic protection effect. The process control of manufacturing Ti-6Al-4V is challenging due to undesired oxygen pick-up and a narrow temperature window for forming. There is a limited formability of Ti-6Al-4V due to thermodynamic equilibrium β-phase fractions of 5 - 10 vol.% at room temperature. Moreover, the manufacturing technique is costly because of high temperature annealing required to process the final product.

[0004] Therefore, ongoing research is being conducted to develop a low-cost (α+β)-titanium alloy that has improved ballistic resistance and/or applicability in other industries such as, e.g., medical devices or aerospace applications.

Summary

[0005] According to an aspect of the disclosure an (α+β)-titanium alloy consists of, in % in weight: Al: 3.0 to 7.0%, (Fe + Cr + Mn): 1.5 to 4.5%, with Cr less than Fe, Mn less than Fe, and Cr less than 1.5%, (Sn + Zr): 1.0 to 5.0%, with Zr less than 0.80, O: 0.03 to 0.35%, and optionally one or more of (V + Mo + Nb + Ta): less than 3.0%, B: less than 1.0%, C: less than 0.08%, N: less than 0.05%, H: less than 0.015%, the balance Ti and incidental impurities.

[0006] According to another aspect of the disclosure a ballistic protection metal sheet is provided which comprises or consists of the (α+β)-titanium alloy as indicated above.

[0007] According to still another aspect of the disclosure a method of manufacturing an (α+β)-titanium alloy product having an alloy composition as set out above is provided. The method comprises melting the alloy composition, hot-rolling the (α+β)-titanium alloy and annealing the hot-rolled (α+β)-titanium alloy.

Brief description of the drawings

[0008]

Figure 1 is a phase diagram displaying the α-phase fraction and the β-phase fraction of conventional Ti-6Al-4V and of Ti-4.5Al-3Fe-1.5Sn-2V according to an example of the disclosure.

Figure 2 is a diagram illustrating flow curves (stress under compression as a function of degree of forming) obtained by compression test measurement during forming at 855°C of conventional Ti-6Al-4V and Ti-4.5Al-3Fe-1.5Sn-2V according to an example of the disclosure.

Figure 3 is a diagram illustrating tensile strength measurement results of conventional Ti-6Al-4V and Ti-4.5Al-3Fe-1.5Sn-2V according to an example of the disclosure.

Figure 4 illustrates exemplary stages of a method of manufacturing an (α+β)-titanium alloy product.

Figure 5 is a schematic perspective view of an exemplary (α+β)-titanium alloy product.

Detailed description

[0009] The titanium base alloys (in the following also referred to as (α+β)-titanium alloys) disclosed herein exhibit high solid solution strengthening and improved β-stabilization. Further, they typically have a relatively low β-transus temperature.

[0010] As a result, improved manufacturing process properties are obtained. For example, energy costs are lowered due to the reduction of process temperature and improved formability. Further, machine wear is reduced due to improved formability.

[0011] Products produced from (α+β)-titanium alloys disclosed herein feature better performance than products made of conventional Ti-6Al-4V. In particular, as a more β-stabilized titanium base alloy can be obtained, a broader range of mechanical properties may be achieved. For example, a higher maximum tensile strength (about +10 - 15% compared to Ti-6Al-4V) or a higher maximum elongation (about +5% compared to Ti-6Al-4V) can be achieved.

[0012] At the microstructural level, lower susceptibility to strain localization than in conventional Ti-6Al-4V has been observed. This effect comes from the lower anisotropy and higher thermal conductivity of the β-phase as compared to the α-phase. Lower susceptibility to strain localization improves the ballistic protection properties of an (α+β)-titanium alloy product as disclosed herein.

[0013] Further, due to the typically lower β-transus temperature than in conventional Ti-6Al-4V, diffusion during the manufacturing process is reduced, resulting in less oxygen uptake and less grain growth. The smaller the grains the higher is the tensile strength of the (α+β)-titanium alloy product.

[0014] The importance and properties of the constituent chemical elements as well as their compositional ranges in the titanium base alloy are described in the following. Throughout this description and the claims, all percentages of the chemical composition are given in percentage in weight (wt.%). The upper, intermediate and lower limits of the individual elements can be freely combined within the compositional ranges set out in the claims.

[0015] Aluminum (Al: 3.0 - 7.0%) is an important α-solid solution strengthening and α-stabilizing element in titanium base alloys. A lower limit is set at 3.0%, otherwise the α-phase may have too low strength. A preferred lower limit is set to 4.0%, because the trade-off of solid-solution strengthening and α-stabilization is optimized in the range above 4.0% (sufficient solid-solution strengthening without losing too much β-stabilization). An upper limit is set to 7.0%, because above 7.0% embrittlement occurs and melting metallurgical production becomes more difficult. A preferred upper limit is set to 5.5%, because hardenability is optionally given, while the α-stabilization effect does not yet exceed an undesirable level. Further, a high solid-solution strengthening effect is available below this preferred upper limit.

[0016] Iron (Fe: 1.5 - 4.5%) is a strong β-stabilizer. Fe segregates strongly but can be produced homogeneously up to 3.0% with ISM (Induction Skull Melting), EBCHM (Electron Beam Cold Hearth Melting), PBCHM (Plasma Beam Cold Hearth Melting) and/or VAR (Vacuum Arc Remelting). An upper limit is set to 4.5%, since above this limit, it is difficult to produce a homogeneous material (due to Fe segregation). A preferred upper limit is set to 3.5% to allow a high degree of β-stabilization and a high solid-strengthening effect. A preferred lower limit is set to 1.9%, where the degree of β-stabilization and the solid-strengthening effect are still sufficient, so that the alloy concept can be pursued by adjusting the other elements. Below a lower limit of 1.5%, the advantage of Fe as an effective and inexpensive β-stabilizer is largely lost.

[0017] Substitution of Fe: Fe may partly be substituted by chromium (Cr) and/or manganese (Mn), which are also β-stabilizers. (Fe + Cr + Mn) equal to or greater than 1.5% also provides sufficient β-phase stabilization. Therefore, the above range for Fe can optionally be replaced or amended by the further condition: (Fe + Cr + Mn): 1.5 - 4.5%, with Cr less than Fe, Mn less than Fe, and Cr less than 1.5%.

[0018] Above 1.5%, the segregation of Cr may be too high. Cr contributions less than 1.0% or 0.5% or 0.2% may be preferred, or, as already mentioned, Cr-free titanium base alloy may be provided. Mn has a similar effect as Fe with respect to β-phase stabilization. With a similar high segregation coefficient as Cr it has an even stronger tendency to form detrimental intermetallic phases. It also evaporates easily in VAR and EBCHM/PBCHM, leading to difficulties or even the exclusion of preferred melting routes. Mn contents of less than 0.5% or 0.1% may be preferred, or in particular a Mn-free titanium base alloy may be advantageous.

[0019] Tin (Sn: 1.0 - 5.0%) is an uncritical alloying element and serves as a neutral solid solution strengthener in both phases. Sn is more or less neutral regarding α- or β-phase stabilization with a slight tendency to stabilize α-phase. Sn stabilizes the detrimental α2-phase (Ti_3Al). An upper limit is set to 5.0% to limit solid-solution strengthening and α- and α2-stabilization. A preferred upper limit is set to 4.0% to provide an optimized range for neutral solid-solution strengthening. A preferred lower limit is set to 1.5% to limit an optimized range for solid-solution strengthening consolidation. Below a lower limit of 1.0% the effect of solid-solution strengthening is largely lost.

[0020] Substitution of Sn: Sn may partly (up to an amount of 0.80) be substituted by zirconium (Zr). Though Sn is slightly α-stabilizing and Zr is slightly β-stabilizing, both elements are nevertheless rather neutral solid solution strengtheners. Therefore, the above range for Sn can optionally be replaced or amended by the further condition: (Sn + Zr): 1.0 - 5.0%, with Zr less than 0.8%, preferably less than 0.5%. As being a substitution element, Zr can be omitted (Zr = 0%). Surprisingly, Sn has been found to be a stronger solid solution strengthener than Zr at concentrations from 1.0 - 5.0%, which is the reason Sn is preferred over Zr. The probable cause is a similar lattice structure between Zr and Ti, which makes the Ti lattice less distorted. In addition, Sn widens the temperature range during hot forming advantageously compared to Zr.

[0021] Vanadium (V: 0.0 - 3.0%) can be used as an additional β-stabilizer and solid solution strengthener. V is more expensive than iron but has no tendency to segregate and is not as strong a β-stabilizer than Fe. V is considered cytotoxic and is preferably avoided for materials in medical technology. An upper limit is set to 3.0% due to price and/or toxicity, depending on the respective application. A preferred upper limit may be set to 2.5% for the same reasons (price, toxicity).

A lower limit is 0.0%, as V is not mandatory since Fe (optionally partly substituted by Cr and/or Mn as mentioned above) can provide sufficient stabilization of the β-phase. For example, in particular for medical technology products, the alloy is preferably free of V.

[0022] Substitution of V: V may partly or fully be substituted by molybdenum (Mo), niobium (Nb), and/or tantalum (Ta), which also act as β-stabilizers. Therefore, the above range for V can optionally be replaced or amended by the further condition: (V + Mo + Nb + Ta): 0.0 - 3.0%. Mo is preferably less than V. In particular, Mo may, e.g., be less than 0.5% or 0.2%. The alloy may also be free of Mo, i.e. Mo = 0%. Although relatively small amounts of Nb and Ta could be acceptable, preferably Nb and Ta are 0%. V is preferred over Mo, Nb and/or Ta because the synergistic effects of solid-solution-strengthening and β-stabilization are best to adjust the desired properties. Larger amounts of Ta and Nb would be necessary for the desired β-stabilization, but this would lead to undesirably high solid-solution-strengthening and thus embrittlement. In contrast, smaller amounts of Mo would be required for the desired β-stabilization, but this would lead to insufficient solid-solution-strengthening.

[0023] Oxygen (O: 0.03 - 0.350) is deliberately added as an interstitial element to improve the strength of the titanium base alloy. Hence, a minimum limit is set to 0.03%. As too much oxygen causes embrittlement at room temperature, an upper limit of 0.35% should not be exceeded. Preferred upper and lower limits are 0.25% and 0.03%, respectively. Oxygen acts as an α-stabilizer.

[0024] Boron (B: 0.0 - 1.00) can be used as an additive for a finer primary grain. This results in a more homogeneous forming and a finer final microstructure. Further, B can reduce oxygen uptake.

[0025] Due to grain refinement, B exhibits a strength-increasing effect. In addition, a preforming process during manufacturing can optionally be simplified or skipped when using B as a grain refining additive since the microstructure is already more homogeneous. An upper limit is set to 1.0% since otherwise brittle effects caused by TiB networks could hinder forming. Below a preferred upper limit of 0.5% the formability is good while strength-enhancing and grain refining advantages for, e.g., improving ballistic protection are still significant. Above a preferred lower limit of 0.08%, grain refining effects are realistic. Even at the lower limit of 0.0%, examples of B-free titanium base alloys according to the disclosure outperformed conventional Ti-6Al-4V in terms of ballistic protection.

[0026] In the following, alloy Ti-4.5Al-3Fe-1.5Sn-2V according to the disclosure is referred to as Ti-4321 and conventional Ti-6Al-4V is referred to as Ti-64. Table 1 summarizes the chemical compositions of titanium base alloys according to the disclosure (upper and lower limits, preferred upper and lower limits as well as the exemplary composition of Ti-4321). As mentioned above, Fe, Sn, and V may be partially or completely replaced by the above substitution elements within the ranges indicated.

Table 1: Chemical compositions of titanium base alloy (in weight percent)

	Al	Fe	Sn	V	B	C	N	O	H	Ti
Upper limit	7.0	4.5	5.0	3.0	1.0	0.08	0.05	0.35	0.015	bal.
Pref. upper limit	5.5	3.5	4.0	2.5	0.5	-	-	0.25	0.01	
Ti-4321	4.5	3.0	1.5	2.0	0.0	0.007	0.01	0.08	0.004	
Pref. lower limit	3.5	1.9	1.5	0.0	0.0	-	-	0.03	0.0	
Lower limit	3.0	1.5	1.0	0.0	0.0	0.0	0.0	0.03	0.0	

[0027] Trace element limits for carbon (C), nitrogen (N) and hydrogen (H) are C: 0.0 - 0.08%, N: 0.0 - 0.05%, and H: 0.0 - 0.015%, respectively. These limits are similar to conventional Ti-64 (Grade 5) and may, e.g., be in compliance with standards (e.g. ASTM B265, AMS 4911 or others, see Table 2). As apparent from Table 1, significantly lower limits may be used, e.g. C: less than 0.06% or 0.02%, N: less than 0.03%, H: less than 0.01%, for example.

[0028] Typically no deliberate addition of C, N and H is used. These elements would act as (undesired) α-stabilizers. In particular, the sum of C + N + O must not exceed 0.4%.

Table 2: Impurity limits according to standards

	ASTM B265C	AMS 4911R	MIL 46077G Class I	MIL 46077G Class II
C	0.08	0.08	0.04	0.08
H	0.015	0.015	0.013	0.015
N	0.05	0.05	0.02	0.05
O	0.2	0.2	0.14	0.3

(continued)

	ASTM B265C	AMS 4911R	MIL 46077G Class I	MIL 46077G Class II
Rest	0.1	0.1	0.1	0.1
In total up to	0.4	0.4	0.4	0.4

[0029] Generally, α-stabilizers are elements that raise the β-transformation temperature and β-stabilizers are elements that lower the β-transformation temperature. The β-transformation temperature T_β (also known as "β-transus temperature" or, briefly, "β-transus") is the lowest temperature where 100% β-phase exists. Only below the β-transus temperature, the α-phase is thermodynamically stable.

[0030] Figure 1 is a phase diagram showing the α-phase fraction and β-phase fraction of conventional Ti-64 and Ti-4321 as a function of temperature (at thermodynamic equilibrium). As mentioned above, Ti-4321 is an illustrative example of a titanium base alloy according to the disclosure.

[0031] $T_{\beta,1}$ denotes the β-transus temperature of Ti-4321 and $T_{\beta,2}$ denotes the β-transus temperature of conventional Ti-64. As apparent from Figure 1, $T_{\beta,1} < T_{\beta,2}$.

[0032] ΔT_1 is the difference between the temperature at phase fraction equality and $T_{\beta,1}$, and ΔT_2 is the difference between the temperature at phase fraction equality and $T_{\beta,2}$. Phase fraction equality means a fraction of 50% α-phase and a fraction of 50% β-phase. As apparent from Figure 1, $\Delta T_1 > \Delta T_2$, meaning that the process window in the α-β region is widened for Ti-4321 compared to Ti-64. In other words, when cooling the titanium base alloy down from the β-region, the phase transition into the α-phase starts at lower temperature and proceeds at a smaller rate for Ti-4321 as compared to Ti-64.

[0033] Thermodynamic equilibrium phase fractions at room temperature are also significantly different for Ti-4321 and conventional Ti-64. While conventional Ti-64 features a ratio $f_\beta/f_\alpha \sim 5/95$ of β-phase fraction f_β and α-phase fraction f_α at room temperature, Ti-4321 has a significantly higher fraction of β-phase alloy at room temperature, namely $f_\beta/f_\alpha \sim 10/90$ or more. Depending on the cooling rate after annealing (see Figure 4), β-phase fractions in Ti-4321 of 15 - 25 vol.% were determined, with 15% for slow, e.g. furnace cooling and 25% in fast, e.g. ambient air cooling. That is, the slower the cooling, the closer the actual phase fractions are to the thermodynamic equilibrium values. This is due to the more effective diffusion with slower cooling.

[0034] For example, slow cooling may be characterized by a cooling rate of 100°C/min or less between 900°C and 700°C. Otherwise, the cooling may be referred to as fast cooling (e.g., ambient air cooling).

[0035] Table 3 illustrates the dependency of the β-transus temperature in °C on the chemical compositions "upper limits" and "lower limits" of Table 1.

Table 3: Minimum and maximum β-transus temperature in °C for chemical compositions of titanium base alloy (in weight percent)

	Al	Fe	Sn	V	B	C	N	O	H	Ti	β-transus
upper limits	7.0	4.5	5.0	3.0	1.0	0.08	0.05	0.35	0.015	bal.	1058.4
lower limits	3.0	1.5	1.0	0.0	0.0	0.0	0.0	0.03	0.0	bal.	848.5

[0036] The chemical composition "upper limits" has a (maximum) β-transus temperature above 1,050°C while the chemical composition "lower limits" has a (minimum) β-transus temperature below 850°C.

[0037] Figure 2 illustrates flow curves (stress under compression in N/mm^2 versus degree of forming φ in 100%, i.e. 1.0 corresponds to $\varphi = 100\%$) obtained by compression test measurements during forming at 855°C of conventional Ti-64 and Ti-4321 according to an example of the disclosure. Significantly easier formability is obtained for Ti-4321 than for Ti-64. More specifically, the required forming force is reduced by at least 30% over the illustrated range of degrees of forming at the same temperature. The easier formability of Ti-4321 is due to optimized phase fractions (i.e. more β-phase). Easier formability is beneficial because it allows either forming at lower temperature or using lower forming force at the same temperature. Both measures (lower temperature and/or lower forming force) permit a reduction in manufacturing costs.

[0038] Figure 3 is a diagram illustrating tensile strength measurement results in longitudinal (L) and transversal (T) direction of a product sample of conventional Ti-64 and a product sample of Ti-4321 in the similar microstructure condition. The tensile strength of Ti-4321 was found to exceed the tensile strength of Ti-64 by about 10%. In particular, a tensile strength of 1,090 MPa in longitudinal direction and 1,155 MPa in transversal direction was measured.

[0039] Further, ballistic VPAM tests (v_{50}, $v_{1/10000}$) were carried out to investigate the ballistic protection effect (VPAM: **V**ereinigung der **P**rüfstellen für **a**ngriffshemmende **M**aterialien und Konstruktionen - Translation: Association of Test Laboratories for Attack Resistant Materials and Constructions). The v_{50} test at test level 9 yields the projectile velocity at 50% failure (i.e. bullet penetration) probability at 20 mm panel thickness. The $v_{1/10000}$ values yields the projectile velocity at 0.01% failure probability, determined from v_{50} test. The tests were carried out and evaluated in accordance with VPAM APR 2006 (APR: **A**llgemeine **P**rüf**R**ichtlinie) of 2010 and TEST GUIDELINE "Bullet resistant plate materials" VPAM - PM Edition 3 as of March 15, 2021. It was found that most of the sample armor plates made of Ti-4321 exhibited ballistic protection of $v_{1/10000} > 805$ m/s, while Ti-64 (Grade 5) sample armor plates were measured at a maximum of $v_{1/10000} < 784$ m/s. Thus, the ballistic protection properties of Ti-4321 exceed those of Ti-64.

[0040] Every damage mechanism in ballistic impact loading causes strain localization. Generally, the more homogeneous the material, the less strain localization occurs.

[0041] The β-phase has fewer anisotropies than the α-phase. Therefore, it is believed that one reason for the better ballistic properties of the titanium base alloys according to the present disclosure is that the proportion of β-phase at room temperature is higher than in Ti-64, resulting in a more homogeneous structure and thus less strain localization. Another reason for the better ballistic properties could be that the β-phase has a better thermal conductivity than the α-phase.

Manufacturing process

[0042] As illustrated in Figure 4, the titanium base alloys according to the present disclosure may, e.g., be produced through ISM (Induction Skull Melting) and one or multiple VAR (Vacuum Arc Remelting) processes. Other possibilities are EBCHM (Electron Beam Cold Hearth Melting) or PBCHM (Plasma Beam Cold Hearth Melting), each followed by one or multiple VAR processes. Further, it is possible to use multiple VAR processes alone (i.e. without initial ISM or EBCHM or PBCHM). The titanium base alloy is then cast into ingots under vacuum. The ingots have a fully β-type microstructure.

[0043] The ingots may then be preformed (e.g. forged). Preforming may be carried out in the β-range (so-called β-forging). For example, preforming may be carried out at ~ 950°C. If the hot-rolling start temperature is in the β-range, preforming may be carried out at about the hot-rolling start temperature, for example.

[0044] The purpose of preforming is to make the ingot more homogeneous. As mentioned above, the preforming process can be simplified or optionally even skipped by adding boron to the titanium base alloy.

[0045] The titanium base alloy (formed as ingots) of the present disclosure is then hot-rolled. In some examples, the hot-rolling start temperature may, e.g., be in the β-range. For example, a hot-rolling start temperature of ~ 950°C may be used.

[0046] In other examples, the hot-rolling start temperature may, e.g., be in the (α+β)-range, i.e. below β-transus. For example, a hot-rolling start temperature of ~ 860°C or even less may be used.

[0047] In both cases (hot-rolling start temperature above or below β-transus), hot-rolling is typically terminated in the (α+β)-range. For example, hot-rolling may terminate at ~ 860°C or even less. Typically, a thickness reduction of equal to or greater than 70% is helpful to adjust the microstructure and mechanical properties of the (α+β)-structure, for example.

[0048] Subsequently, the hot-rolled titanium base alloy is annealed. In some examples, annealing is carried out in the β-range. For example, annealing may be carried out at ~ 950°C. The duration of annealing (after complete through-heating of the alloy) may, e.g., be about 45 to 90 minutes, more preferable 45 to 60 minutes. Annealing in the β-range is also referred to as "β-annealing".

[0049] In other examples, annealing is carried out in the (α+β)-range, i.e. below β-transus. In this case, annealing may be carried out temperatures between, e.g., ~ 700°C and ~ 900°C. Preferable, annealing may be carried out at temperatures equal to or less than ~ 880°C or ~ 860°C, for example. The duration of annealing (after complete through-heating of the alloy) may, e.g., be approximately 60 to 90 minutes or even longer. Annealing in the (α+β)-range is also referred to as "solution annealing".

[0050] Possible annealing processes also include stress relief annealing or mill annealing, for example.

[0051] The type of annealing (e.g., β-annealing or solution annealing) has implications on the microstructure of the (α+β)-titanium alloy product to be produced. β-annealing typically results in a lamellar microstructure, e.g. in a coarse lamellar microstructure 420 or in a fine lamellar microstructure 422. On the other hand, solution annealing results in a bimodal microstructure 440 or in a globular microstructure 442.

[0052] The lamellar microstructure 420, 422 cannot be transformed into a bimodal microstructure 440 or into a globular microstructure 442 by any subsequent heat treatment. For some applications such as ballistic protection, a bimodal microstructure 440 or, in particular, a globular microstructure 442 is preferred. Thus, in some examples, solution annealing may be preferred over β-annealing.

[0053] After annealing, the annealed titanium base alloy is cooled down to room temperature. In some examples ambient air cooling may be used. In particular, ambient air cooling may be used for bimodal microstructures 442. That way, a high strength of about 1,170 MPa or more was achieved (e.g., for a panel thickness of about 20 mm), for example.

[0054] In other examples, the annealed titanium base alloy may be cooled down to room temperature at a rate slower than air cooling. Slow cooling may be performed in a furnace configured to set a cooling rate smaller than the cooling rate of ambient air. Especially for globular microstructures 442, slower cooling than in ambient air can be used. In this way, a high ductility (e.g., about 14.30 or more) was achieved.

[0055] Generally, a lower temperature at all process steps (e.g., about 100°C less at forging and/or hot rolling and/or annealing for microstructure adjustment) compared to conventional Ti-64 manufacturing can be achieved. This lowers diffusion and may reduce unwanted oxygen uptake (having an embrittlement effect). At all process steps, lower temperatures lead to a reduction in grain growth, which has a positive effect on strength. Further, as forging and hot rolling forces may be reduced, machines are less worn out and/or life span of machines may increase. Lower temperatures may also provide energy and cost savings at all process steps.

[0056] Referring to Figure 5, titanium base alloys with the above composition and/or manufacturing process can be used, for example, as ballistic protection sheets such as armor plates 500 due to their high ballistic protection effect.

EXAMPLES

[0057] In the following examples, exemplary titanium base alloys according to the present disclosure are compared to reference titanium base alloys not according to the present disclosure. The chemical compositions of the exemplary titanium base alloys (Examples 1 - 9) and reference titanium base alloy (Examples 10 - 13) are presented in Table 4 and Table 5, respectively. All of the compositions were induction skull melted (ISM), subsequently two times vacuum arc remelted (VAR) and conventionally casted into ingots under vacuum. The ingots were heated up to about 960°C, forged and later hot-rolled into 20 mm plates at a temperature below β-transus. The plates were cut in order to obtain specimens (e.g., smaller plates) for solution annealing, metallographic characterization, tensile tests, hardness tests, and ballistic impact tests (v_{50} test and $v_{1/10000}$ analysis) . The Vickers hardness was measured in accordance with the EN ISO 6507-1 standard.

Table 4: Examples - chemical composition (in weight percent) and properties of titanium base alloys according to the present disclosure

	Al	Fe	Sn	V	B	C	N	O	H	Ti	T_β [°C]	Hard [VH]	V_{50} [m/s]	$V_{1/10000}$ [m/s]
Ex. 1	4.5	3.0	1.5	2.0	0.0	0.01	0.01	0.12	0.008	bal.	928	360	840	833
Ex. 2	4.5	1.5	3.0	2.0	0.0	0.01	0.01	0.12	0.008		958	360	840	815
Ex. 3	5.0	2.0	2.0	2.0	0.0	0.01	0.01	0.12	0.008		956	330	825	780
Ex. 4	5.0	2.0	2.0	2.0	0.1	0.01	0.01	0.12	0.008		956	345	830	795
Ex. 5	5.0	2.0	2.0	2.0	0.5	0.01	0.01	0.12	0.008		956	360	835	820
Ex. 6	4.5	3.0	1.5	2.0	0.1	0.01	0.01	0.12	0.008		928	370	850	843
Ex. 7	4.5	3.0	1.5	2.0	0.5	0.01	0.01	0.12	0.008		928	395	850	843
Ex. 8	4.0	3.5	1.5	0.0	0.1	0.01	0.01	0.12	0.008		934	390	840	833
Ex. 9	5.5	3.0	3.0	2.0	0.5	0.01	0.01	0.12	0.008		956	410	835	820

[0058] Examples 1, 6 and 7 relate to Ti-4321 with different amounts of B added. It is apparent that the addition of B improves the ballistic properties as well as the Vickers hardness of the titanium base alloy. The β-transus temperature is not significantly affected by addition of B.

[0059] In the examples of Table 4, Fe, Sn and V were not substituted by any of the substitution elements set out above. However, research considerations suggest that substitutions within the ranges indicated above are likely to (at least partially) preserve the beneficial effects according to the present disclosure.

Table 5: Examples - chemical composition (in weight percent) and properties of titanium base alloys not according to the present disclosure

	Al	**Fe**	**Sn**	**V**	**B**	**C**	**N**	**O**	**H**	**Ti**	**T_β [°C]**	**β-fraction [vol%]**
Ex. 10	**8**	3	1.5	2	0	0.01	0.01	0.12	0.008	bal.	1002.06	6
Ex. 11	4.5	**5**	1.5	2	0	0.01	0.01	0.12	0.008		897.41	24
Ex. 12	4.5	3	**0**	2	0	0.01	0.01	0.12	0.008		921.91	22
Ex. 13	4.5	2	2	**4**	0	0.01	0.01	0.12	0.008		922.11	18

[0060] In Table 5, composition values that fall outside the ranges are in bold. In Example 10, too much Al is present. As a result, the titanium base alloy is difficult to produce, because Al evaporates. Further, this titanium alloy features too high embrittlement because of formation of the brittle α2-phase. Such titanium base alloy is difficult to produce in terms of process technology. In Example 11, too much Fe is present. This results in strong Fe segregation and poor creep resistance due to rapid diffusion. In Example 12, too little Sn has been added. As a result, neutral solidification is missing (i.e. Sn solidifies α-phase and β-phase without stabilizing a certain phases). In Example 13, too much V is present. Such high V content would cancel out the cost savings and increase cytotoxicity (therefore, omitting V from the alloy may also be preferable, for example).

[0061] Although specific embodiments have been illustrated and described herein, it will be appreciated by those of ordinary skill in the art that a variety of alternate and/or equivalent implementations may be substituted for the specific embodiments shown and described without departing from the scope of the present invention. This application is intended to cover any adaptations or variations of the specific embodiments discussed herein. Therefore, it is intended that this invention be limited only by the claims and the equivalents thereof.

Claims

1. An (α+β)-titanium alloy consisting of, in % in weight:

Al: 3.0 to 7.0%,
Fe + Cr + Mn: 1.5 to 4.5%, with Cr less than Fe, Mn less than Fe,
and Cr less than 1.5%,
Sn + Zr: 1.0 to 5.0%, with Zr less than 0.80,
O: 0.03 to 0.35%,
and optionally one or more of
V + Mo + Nb + Ta: less than 3.0%,
B: less than 1.0%,
C: less than 0.08%,N: less than 0.05%,
H: less than 0.015%,
the balance Ti and incidental impurities.

2. The (α+β)-titanium alloy of claim 1, fulfilling the following requirement:
Sn: 1.0 to 5.0%.

3. The (α+β)-titanium alloy of claim 1, fulfilling the following requirement:

B: 0.08 to 0.5%.

4. The ($\alpha+\beta$)-titanium alloy of any of the preceding claims, fulfilling at least one of the following requirements:

Al: 3.5 to 5.5%,
Fe + Cr + Mn: 1.9 to 3.5%,
Sn + Zr: 1.5 to 4.0%,
O: 0.03 to 0.25%.

5. The ($\alpha+\beta$)-titanium alloy of any of the preceding claims, fulfilling at least one of the following requirements:

Cr: less than Fe, and/or Cr less than 1.0% or 0.5% or 0.2% or
Cr = 0%,
Mn: less than Fe, and/or Mn less than 0.5% or 0.1% or Mn = 0%.

6. The ($\alpha+\beta$)-titanium alloy of any of the preceding claims, fulfilling the following requirement:
Zr: less than 0.5%, or Zr = 0%.

7. The ($\alpha+\beta$)-titanium alloy of any of the preceding claims, fulfilling the following requirement:
V: less than 2.5%, or V = 0%.

8. The ($\alpha+\beta$)-titanium alloy of any of the preceding claims, fulfilling at least one of the following requirements:
Mo: less than V, and/or Mo less than 0.5% or 0.2% or Mo = 0%.

9. The ($\alpha+\beta$)-titanium alloy of any of the preceding claims, fulfilling at least one of the following requirements:

Nb = 0%,
Ta = 0%,
H: less than 0.01%.

10. A ballistic protection metal sheet comprising the ($\alpha+\beta$)-titanium alloy of any of the preceding claims.

11. A method of manufacturing an ($\alpha+\beta$)-titanium alloy product, the method comprising:

providing an ($\alpha+\beta$)-titanium alloy composition of, in % in weight:

Al: 3.0 to 7.0%,
Fe + Cr + Mn: 1.5 to 4.5%, with Cr less than Fe, Mn less than Fe, and Cr less than 1.5%,
Sn + Zr: 1.0 to 5.0%, with Zr less than 0.80,
O: 0.03 to 0.35%,
and optionally one or more of
V + Mo + Nb + Ta: less than 3.0%,
B: less than 1.0%,
C: less than 0.08%,
N: less than 0.05%,
H: less than 0.015%,
the balance Ti and incidental impurities;

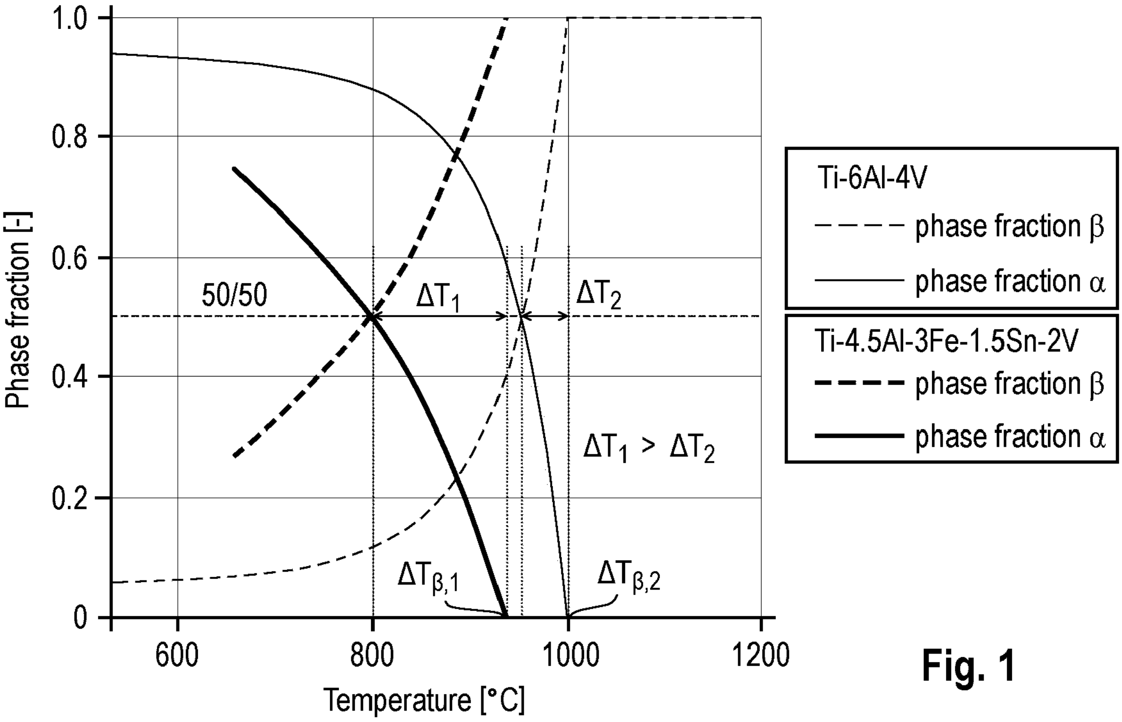
melting the ($\alpha+\beta$)-titanium alloy composition;
hot-rolling the ($\alpha+\beta$)-titanium alloy; and
annealing the hot-rolled ($\alpha+\beta$)-titanium alloy.

12. The method of claim 11, wherein melting the ($\alpha+\beta$)-titanium alloy composition comprises one or more processes of the group consisting of Induction Skull Melting, Electron Beam Cold Hearth Melting, Plasma Beam Cold Hearth Melting and one or multiple Vacuum Arc Remelting processes.

13. The method of claim 11 or 12, wherein hot-rolling starts at a hot-rolling start temperature which is above β-transus temperature.

14. The method of one or more of claims 11 to 13, wherein annealing is carried out at a temperature above β-transus temperature.

15. The method of one or more of claims 11 to 13, wherein annealing is carried out at a temperature below β-transus temperature, in particular below 860°C.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0.6
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Temperature [°C]
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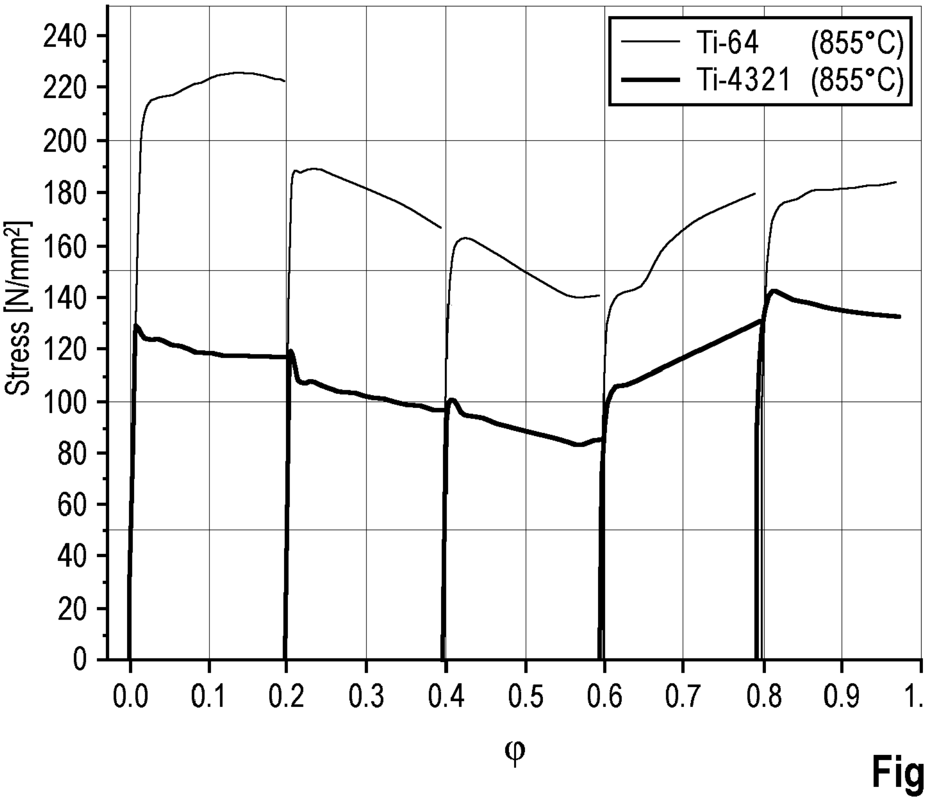
ΔT1
ΔT2
ΔT1 > ΔT2
ΔTβ,1
ΔTβ,2
Ti-6Al-4V
phase fraction β
phase fraction α
Ti-4.5Al-3Fe-1.5Sn-2V
phase fraction β
phase fraction α

Fig. 1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220
200
180
160
140
120
100
80
60
40
20
0
Stress [N/mm²]
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
φ
Ti-64 (855°C)
Ti-4321 (855°C)

Fig. 2

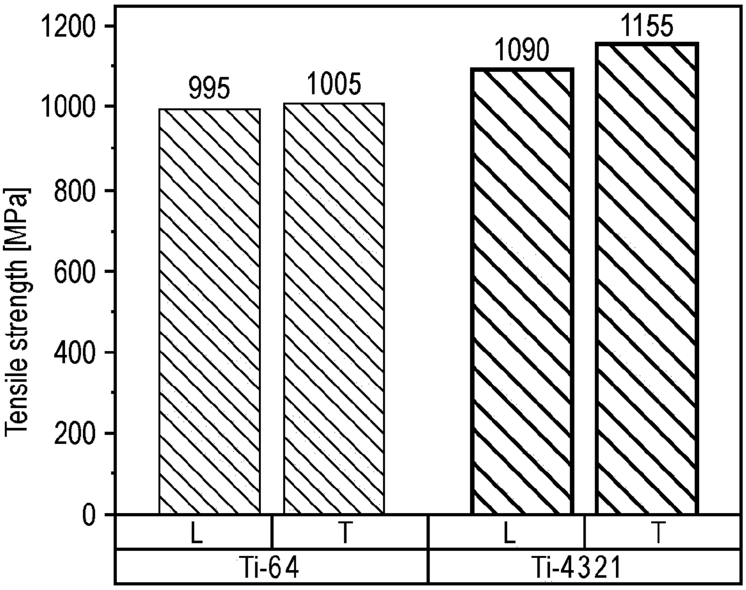

Fig. 3

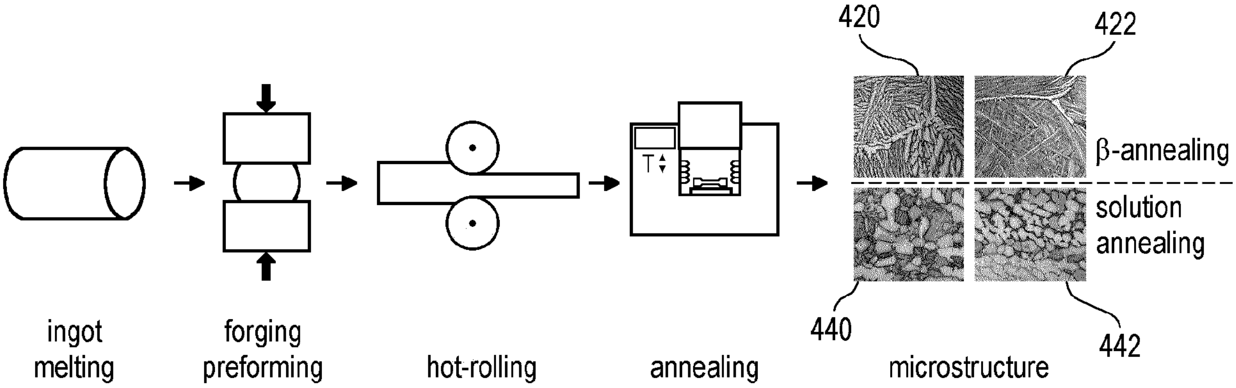

Fig. 4

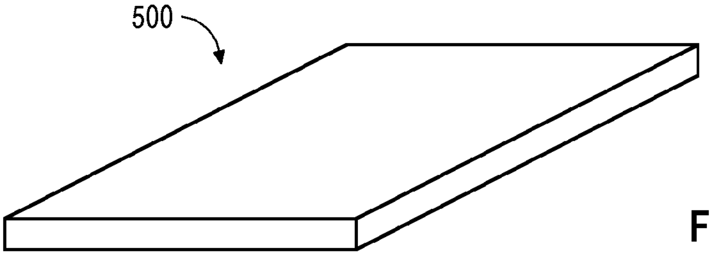

Fig. 5

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EUROPEAN SEARCH REPORT

Application Number
EP 23 16 0675

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Y	* paragraph [0014] * * paragraph [0088] - paragraph [0109] * * tables 1-5 * * examples 1-3; table 1 * * figure 1 * * claims 1-7 * -----	3	
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Y	* paragraph [0045] - paragraph [0046] * * No. 10; table 1 * * claims 1-2 * ----- -/--	3	

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	23 July 2023	Neibecker, Pascal

CATEGORY OF CITED DOCUMENTS

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EUROPEAN SEARCH REPORT

Application Number
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