(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 974 082 A1**

(12) EUROPEAN PATENT APPLICATION

published in accordance with Art. 153(4) EPC

(43) Date of publication:
30.03.2022 Bulletin 2022/13

(21) Application number: **20810724.3**

(22) Date of filing: **18.03.2020**

(51) International Patent Classification (IPC):
B21J 5/00 $^{(2006.01)}$ ***C22C 14/00*** $^{(2006.01)}$
C22F 1/00 $^{(2006.01)}$ ***C22F 1/18*** $^{(2006.01)}$

(52) Cooperative Patent Classification (CPC):
B21J 5/00; C22C 14/00; C22F 1/18; C22F 1/00

(86) International application number:
PCT/JP2020/011936

(87) International publication number:
WO 2020/235201 (26.11.2020 Gazette 2020/48)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **23.05.2019 JP 2019096652**

(71) Applicant: **IHI Corporation**
Tokyo 135-8710 (JP)

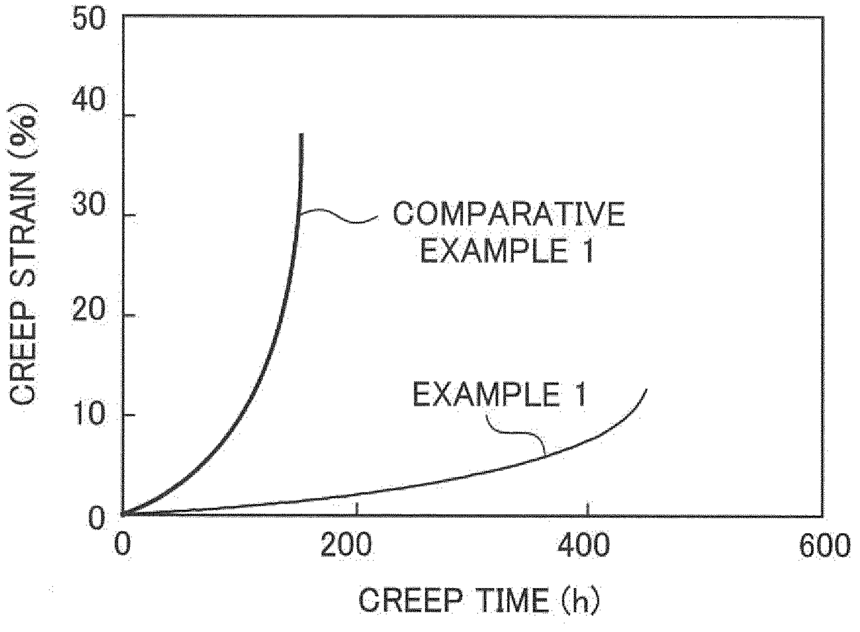
(72) Inventor: **KUBUSHIRO, Keiji**
Tokyo 135-8710 (JP)

(74) Representative: **MERH-IP Matias Erny Reichl Hoffmann**
Patentanwälte PartG mbB
Paul-Heyse-Strasse 29
80336 München (DE)

(54) TIAL ALLOY AND PRODUCTION METHOD THEREFOR

(57) A TiAl alloy contains 48 at% or more and 50 at% or less of Al, 3 at% or more and 5 at% or less of Nb, 0.1 at% or more and 0.3 at% or less of B, and the balance being Ti and inevitable impurities.

FIG. 8



Printed by Jouve, 75001 PARIS (FR)

Description

[Technical Field]

[0001] The present disclosure relates to a TiAl alloy and a method of manufacturing the same.

[Background Art]

[0002] A TiAl (titanium aluminide) alloy is an alloy formed of an intermetallic compound of Ti and A1. The TiAl alloy is excellent in the heat resistance, and has a lighter weight and larger specific strength than an Ni-base alloy, and thus, is applied to aircraft engine components such as turbine blades. For such the TiAl alloy, a TiAl alloy containing Cr and Nb is used (see Patent Literature 1).

[Citation List]

[Patent Literature]

[0003] [PTL 1] Japanese Patent Application Publication No. 2013-209750

[Summary of Invention]

[Technical Problem]

[0004] In order to reduce the weight of TiAl alloy parts such as turbine blades, to increase the specific strength of the TiAl alloy by increasing the strength of the TiAl alloy is needed. However, in a conventional TiAl alloy, it is difficult to increase the strength by improving the mechanical strength and the ductility in a good balance, and if the ductility is increased, the mechanical strength may degrade.

[0005] Therefore, an object of the present disclosure is to provide a TiAl alloy capable of improving the mechanical strength and the ductility of the TiAl alloy in a good balance, and a method of manufacturing the same.

[Solution to Problem]

[0006] A TiAl alloy according to the present disclosure contains 48 at% or more and 50 at% or less of Al, 3 at% or more and 5 at% or less of Nb, 0.1 at% or more and 0.3 at% or less of B, and the balance being Ti and inevitable impurities.

[0007] In the TiAl alloy according to the present disclosure, the content of Al may be 49 at%.

[0008] In the TiAl alloy according to the present disclosure, a metal structure may be formed of lamellar grains and γ grains, and may be free of the segregation of Nb.

[0009] In the TiAl alloy according to the present disclosure, a volume fraction of the lamellar grains may be 80 volume % or more, relative to a total of the volume fraction of the lamellar grain and the volume fraction of the γ grain being 100 volume %.

[0010] In the TiAl alloy according to the present disclosure, Vickers hardness at a room temperature may be 200 HV or more.

[0011] In the TiAl alloy according to the present disclosure, room temperature ultimate tensile strength may be 400 MPa or more and room temperature tensile fracture strain may be 1.0 % or more.

[0012] In the TiAl alloy according to the present disclosure, creep strain after the elapse of 200 hours may be 2 % or less, when a temperature is 800 °C and applied stress is 150 MPa.

[0013] A method of manufacturing a TiAl alloy according to the present disclosure includes a casting step of casting a TiAl alloy raw material which contains 48 at% or more and 50 at% or less of Al, 3 at% or more and 5 at% or less of Nb, 0.1 at% or more and 0.3 at% or less of B, and the balance being Ti and inevitable impurities.

[0014] In the method of manufacturing the TiAl alloy according to the present disclosure, in the casting step, a solidification process may pass through an α single phase region.

[0015] The method of manufacturing the TiAl alloy according to the present disclosure may include a hot isostatic pressing process step for performing a hot isostatic pressing process of applying hot isostatic pressing to the cast TiAl alloy at a temperature range from 1250 °C or higher to 1350 °C or lower, for a hour range from 1 hour or more to 5 hours or less, at an applied stress range from 158 MPa or higher to 186 MPa or lower, and then furnace cooling the cast TiAl alloy subjected to the hot isostatic pressing to 900 °C, followed by rapid cooling of the cast TiAl alloy subjected to the hot isostatic pressing from 900 °C.

[0016] The method of manufacturing the TiAl alloy according to the present disclosure may include a stress relieving step of relieving stress by holding the TiAl alloy subjected to the hot isostatic pressing process at a temperature range from 800 °C or higher to 950 °C or lower for a hour range from 1 hour or more to 5 hours or less.

[0017] According to the thus-configured TiAl alloy and the thus-configured method of manufacturing the same, the mechanical strength and the ductility of the TiAl alloy can be improved in a good balance.

[Brief Description of Drawings]

[0018]

[Fig. 1]
Fig. 1 shows a constitution of a turbine blade in an embodiment of the present disclosure.
[Fig. 2]
Fig. 2 is a graph showing results of tensile tests in an embodiment of the present disclosure.
[Fig. 3]
Fig. 3 is photographs showing results of the observation of metal structures of TiAl alloys of Reference Examples 4 to 8, in an embodiment of the present disclosure.
[Fig. 4]
Fig. 4 is photographs showing results of the observation of metal structures of TiAl alloys of Examples 2 to 4, and Reference Examples 9 and 10, in an embodiment of the present disclosure.
[Fig. 5]
Fig. 5 is a graph showing results of the measurement of Vickers hardness of TiAl alloys before being subjected to hot isostatic pressing process, in an embodiment of the present disclosure.
[Fig. 6]
Fig. 6 is a graph showing results of the measurement of Vickers hardness of TiAl alloys subjected to hot isostatic pressing process, in an embodiment of the present disclosure.
[Fig. 7]
Fig. 7 is a graph showing results of tensile tests in an embodiment of the present disclosure.
[Fig. 8]
Fig. 8 is a graph showing results of creep tests, in an embodiment of the present disclosure.
[Fig. 9]
Fig. 9 is photographs showing results of the observation of cross-sectional areas after performing oxidation tests, in an embodiment of the present disclosure.

[Description of Embodiments]

[0019] An embodiment of the present disclosure will be described in detail below with reference to the drawings. A TiAl (titanium aluminide) alloy according to an embodiment of the present disclosure contains 48 at% or more and 50 at% or less of Al, 3 at% or more and 5 at% or less of Nb, 0.1 at% or more and 0.3 at% or less of B, and the balance being Ti and inevitable impurities. Next, the reason why a composition range of each alloy component contained in the TiAl alloy is limited will be explained.

[0020] Al (aluminium) has a function of improving the mechanical strength and the ductility such as the room temperature ductility. The content of Al is in a range from 48 at% or more to 50 at% or less. The ductility degrades if the content of Al is less than 48 at%. The ductility degrades if the content of Al is more than 50 at%. Further, if the content of Al is more than 50 at%, a solidification process changes from an α single phase region (α solidification) to a γ single phase region (γ solidification), and thus, a columnar crystal is formed, and there is a possibility that the anisotropy occurs. By setting the content of Al in a range from 48 at% or more to 50 at% or less, the solidification process can be in the α single phase region (α solidification), and this can suppresses the anisotropy. Further, the mechanical strength and the ductility can be further improved by setting the content of Al to 49 at%.

[0021] Nb (niobium) has a function of improving the oxidation resistance and the mechanical strength. The content of Nb is in a range from 3 at% or more to 5 at% or less. If the content of Nb is less than 3 at%, the oxidation resistance and the high-temperature strength degrade. If the content of Nb is more than 5 at%, the ductility such as the room temperature ductility degrades. Further, if the content of Nb is 5 at% or less, the segregation of Nb can be suppressed. The occurrence of the segregation of Nb may degrade the mechanical strength and the ductility.

[0022] B (boron) has a function of enhancing the ductility such as the room temperature ductility by refining crystal grains. The content of B is in a range from 0.1 at% or more to 0.3 at% or less. If the content of B is less than 0.1 at%, the crystal grains are coarsened and the ductility degrades. If the content of B is more than 0.3 at%, impact characteristics may be degraded. By setting the content of B in a range from 0.1 at% or more to 0.3 at% or less, the TiAl alloy comes to be formed of fine crystal grains with a crystal grain size of 200 μm or less, and accordingly, the ductility can be improved.

[0023] B has a function of improving the mechanical strength by precipitating fine borides in the crystal grains through the application of a hot isostatic pressing process which will be described later. The fine borides are formed by including borides with a grain size of 0.1 μm or less. The fine borides are formed of TiB, TiB_2 or the like. The precipitation of the fine borides in the crystal grains can improve the mechanical strength such as the tensile strength, the fatigue strength, and the creep strength.

[0024] The balance of the TiAl alloy is Ti and inevitable impurities. The inevitable impurities are impurities that may be mixed even if a user has no intension to add. The TiAl alloy does not contain Cr (chromium), and therefore, the degradation in the mechanical strength can be suppressed. The TiAl alloy does not contain V (vanadium) either, and therefore, the degradation in the mechanical strength and the oxidation resistance can be suppressed. Further, the TiAl alloy does not contain Mo (molybdenum) either, and thus, the degradation in the specific strength can be suppressed.

[0025] Next, a method of manufacturing a TiAl alloy according to an embodiment of the present disclosure will be described.

[0026] A method of manufacturing a TiAl alloy includes a casting step of melting and casting a TiAl alloy raw material which contains 48 at% or more and 50 at% or less of Al, 3 at% or more and 5 at% or less of Nb, 0.1 at% or more and 0.3 at% or less of B, and the balance being Ti and inevitable impurities. The TiAl alloy raw material is melted in a vacuum induction furnace or the like and cast to form an ingot or the like. The casting of the TiAl alloy raw material may use a casting system which is used for casting a general metallic material.

[0027] A solidification temperature of the TiAl alloy is lower than that of a conventional TiAl alloy, and thus, it is possible to improve running properties during casting. This enables the formation of a TiAl alloy part such as a turbine blade into a net-shape or a near-net-shape, and accordingly, it is possible to reduce a manufacturing cost. Further, according to the TiAl alloy, to take the superheat is not needed, and accordingly, the castability is improved. In this TiAl alloy, the solidification process passes through the α single phase region (α solidification). This enables the prevention of the occurrence of columnar crystals in the TiAl alloy and the suppression of the anisotropy.

[0028] The method of manufacturing the TiAl alloy may include a hot isostatic pressing process step for performing a hot isostatic pressing process of applying hot isostatic pressing (HIP) to a cast TiAl alloy at a temperature range from 1250 °C or higher to 1350 °C or lower, for a hour range from 1 hour or more to 5 hours or less, at an applied stress range from 158 MPa or higher to 186 MPa or lower, and then, furnace cooling the cast TiAl alloy subjected to the hot isostatic pressing to 900 °C, followed by rapid cooling of the cast TiAl alloy from 900 °C. By performing the hot isostatic pressing process, it is possible to suppress casting defects such as voids and control a metal structure.

[0029] More specifically, by applying the hot isostatic pressing to the cast TiAl alloy at a temperature range from 1250 °C or higher to 1350 °C or lower, for a hour range from 1 hour or more to 5 hours or less, and at an applied stress range from 158 MPa or higher to 186 MPa or lower, it is possible to suppress mainly casting defects including internal defects such as voids caused to the cast TiAl alloy. After performing the hot isostatic pressing to the cast TiAl alloy, pressure is relieved, the cast TiAl alloy subjected to the hot isostatic pressing is furnace cooled to 900 °C, and the cast TiAl alloy subjected to the hot isostatic pressing is rapidly cooled from 900 °C, and accordingly, the metal structure can be mainly controlled. The rapid cooling from 900 °C may be performed at a cooling rate which is equal to or higher than that of air cooling, and can be performed by gas fan cooling or the like.

[0030] The method of manufacturing the TiAl alloy may include a stress relieving step of relieving stress by holding the TiAl alloy subjected to the hot isostatic pressing process at a temperature range from 800 °C or higher to 950 °C or lower, for a hour range from 1 hour or more to 5 hours or less. Residual stress and the like can be relieved by heattreating the TiAl alloy subjected to the hot isostatic pressing process to relieve stress. This can further improve the ductility of the TiAl alloy.

[0031] In order to prevent the oxidation, the hot isostatic pressing process and the stress relief may be performed in a vacuum atmosphere, or an inert gas atmosphere with gas such as argon gas. For the hot isostatic pressing, HIP equipment or the like which is used for the hot isostatic pressing of a general metallic material can be used. For the stress relief, an atmosphere furnace or the like which is used for stress relief annealing of a general metallic material can be used.

[0032] Next, the metal structure of the TiAl alloy will be described. The metal structure of the TiAl alloy is formed of fine crystal grains with a crystal grain size of 200 μm or less. This can improve the ductility of the TiAl alloy. Further, the metal structure of the TiAl alloy is formed of lamellar grains and γ grains, and is free of the segregation of Nb. The lamellar grains are formed by regularly arranging α_2 phases formed of Ti_3Al and γ phases formed of TiAl in a layered structure. The γ grains are formed of TiAl. Boride with a grain size of 0.1 μm or less is contained in the γ grains. The boride is formed of TiB, TiB_2 or the like in a needle shape or the like.

[0033] The lamellar grains can improve the mechanical strength such as the tensile strength, the fatigue strength, and the creep strength. The γ grains can improve the ductility and the high-temperature strength. The fine borides with a grain size of 0.1 μm or less can improve the mechanical strength. Relative to a total of the volume fraction of the lamellar grain and the volume fraction of the γ grain being 100 volume %, a volume fraction of the lamellar grains may be 80 volume % or more, and the balance may be γ grains. The metal structure of the TiAl alloy is mainly formed of the lamellar grains, and thus, the mechanical strength can be improved. Further, the metal structure of the TiAl alloy is free of the segregation of Nb, and thus, the degradation in the mechanical strength and the ductility can be suppressed.

[0034] Next, mechanical characteristics of the TiAl alloy according to the embodiment of the present disclosure will be described. The mechanical characteristics of the TiAl alloy at room temperature may be such that Vickers hardness at room temperature is 200 HV or more, when Vickers hardness is measured in accordance with JIS, ASTM, and the like. Further, when tensile tests are performed in accordance with JIS, ASTM, and the like, the mechanical characteristics of the TiAl alloy at room temperature may be such that room temperature ultimate tensile strength is 400 MPa or more and room temperature tensile fracture strain is 1.0 % or more. The high temperature creep characteristics of the TiAl alloy may be such that the creep strain after the elapse of 200 hours is 2 % or less, when creep tests are performed in accordance with JIS, ASTM, and the like under a condition where a temperature is 800 °C and applied stress is 150 MPa. Further, the high temperature creep characteristics of the TiAl alloy may be such that the creep strain after the elapse of 400 hours is 7 % or less, when tests are performed under a condition where a temperature is 800 °C and applied stress is 150 MPa.

[0035] The TiAl alloy according to the embodiment of the present disclosure can be applied to a turbine blade or the like of an aircraft engine component. Fig. 1 is a diagram showing a constitution of a turbine blade 10. The TiAl alloy has high mechanical strength such as high-temperature strength, and thus, the heat resistance of the turbine blade 10 can be improved. Further, the TiAl alloy has excellent room temperature ductility, and thus, damage to the turbine blade 10 can be suppressed even when the turbine blade 10 is assembled or fitted.

[0036] The above described TiAl alloy contains 48 at% or more and 50 at% or less of Al, 3 at% or more and 5 at% or less of Nb, 0.1 at% or more and 0.3 at% or less of B, and the balance being Ti and inevitable impurities. Accordingly, the mechanical strength and the ductility of the TiAl alloy can be improved in a good balance.

[0037] The above described method of manufacturing the TiAl alloy includes a casting step of casting the TiAl alloy raw material which contains 48 at% or more and 50 at% or less of Al, 1 at% or more and 3 at% or less of Nb, 0.1 at% or more and 0.3 at% or less of B, and the balance being Ti and inevitable impurities. As a result, the TiAl alloy with the mechanical strength and the ductility which are improved in a good balance can be manufactured, and also the castability can be improved because running properties are favorable.

[Examples]

[0038] First, TiAl alloys of Examples 1 to 4, Reference Examples 1 to 10, and Comparative Example 1 will be described. An alloy composition of each TiAl alloy is shown in Table 1.

[0039]

[Table 1]

	ALLOY COMPOSITION (at%)				
	Al	Nb	B	Cr	TI AND INEVITABLE IMPURITIES
EXAMPLE 1	49.5	4	0.2	-	BALANCE
EXAMPLE 2	48	4	0.1	-	BALANCE
EXAMPLE 3	49	4	0.1	-	BALANCE
EXAMPLE 4	50	4	0.1	-	BALANCE
REFERENCE EXAMPLE 1	48	4	-	-	BALANCE
REFERENCE EXAMPLE 2	49	4	-	-	BALANCE
REFERENCE EXAMPLE 3	50	4	-	-	BALANCE
REFERENCE EXAMPLE 4	48	-	0.1	-	BALANCE
REFERENCE EXAMPLE 5	49	-	0.1	-	BALANCE
REFERENCE EXAMPLE 6	50	-	0.1	-	BALANCE
REFERENCE EXAMPLE 7	51	-	0.1	-	BALANCE
REFERENCE EXAMPLE 8	52	-	0.1	-	BALANCE
REFERENCE EXAMPLE 9	51	4	0.1	-	BALANCE
REFERENCE EXAMPLE 10	52	4	0.1	-	BALANCE

(continued)

	ALLOY COMPOSITION (at%)				
	Al	Nb	B	Cr	TI AND INEVITABLE IMPURITIES
COMPARATIVE EXAMPLE 1	48	2	-	2	BALANCE

[0040] The Tial alloy of Example 1 contained 49.5 at% of Al, 4 at% of Nb, 0.2 at% of B, and the balance being Ti and inevitable impurities. The Tial alloy of Example 2 contained 48 at% ofAl, 4 at% of Nb, 0.1 at% of B, and the balance being Ti and inevitable impurities. The TiAl alloy of Example 4 contained 50 at% of Al, 4 at% of Nb, 0.1 at% of B, and the balance being Ti and inevitable impurities.

[0041] The TiAl alloys in Reference Examples 1 to 3 were set as ternary TiAl alloys containing Nb, the content of Nb was 4 at%, and the content of Al was changed from 48 at% to 50 at%. The TiAl alloys in Reference Examples 4 to 8 were set as ternary TiAl alloys containing B, the content of B was 0.1 at%, and the content of Al was changed from 48 at% to 52 at%. The TiAl alloys in Reference Examples 9 and 10 were set as quaternary TiAl alloys containing Nb and B, the content of Nb was 4 at%, the content of B was 0.1 at%, and the content of Al was changed from 51 at% to 52 at%. The TiAl alloy of Comparative Example 1 contained 48 at% of Al, 2 at% of Nb, 2 at% of Cr, and the balance being Ti and inevitable impurities.

[0042] Each TiAl alloy raw material of each alloy composition shown in Table 1 was melted in a high-frequency vacuum melting furnace and cast to form an ingot of each TiAl alloy of each alloy composition. Each TiAl alloy was casted, and then, is subjected to the hot isostatic pressing process. In the hot isostatic pressing process, the cast TiAl alloy was subjected to the hot isostatic pressing at a temperature of 1300 ± 14 °C, for an hour of 3 ± 0.1 hours, and at applied stress of 172 ± 14 MPa, and then, the cast TiAl alloy subjected to the hot isostatic pressing was furnace cooled to 900 °C, followed by rapid cooling of the cast TiAl alloy subjected to the hot isostatic pressing from 900 °C by gas fan cooling.

[0043] Effects of Al in the TiAl alloys were evaluated. Tensile tests were performed at room temperature for the TiAl alloys of Reference Examples 1 to 3. The tensile tests were performed in accordance with ASTM E8. Fig. 2 is a graph showing results of the tensile tests. In the graph of Fig. 2, a horizontal axis represents the content of Al, a vertical axis represents the strain, and Reference Examples 1 to 3 are shown in white diamond shapes. Strain indicates fracture strain. From the graph of Fig. 2, it was found that the room temperature ductility degrades if the content of Al is less than 48 at%, or if the content of Al is more than 50 at%. Further, the strain of Reference Example 2 was larger than that of Reference Examples 1 and 3. This indicates that the room temperature ductility becomes higher if the content of Al is 49 at%.

[0044] The metal structures of the TiAl alloys were evaluated. The metal structures of the TiAl alloys of Examples 2 to 4 and Reference Examples 4 to 10 were observed. The metal structures were observed by using an optical microscope. Fig. 3 is photographs showing results of the observation of the metal structures of the TiAl alloys of Reference Examples 4 to 8, that is, Fig. 3(a) is a photograph of Reference Example 4, Fig. 3(b) is a photograph of Reference Example 5, Fig. 3(c) is a photograph of Reference Example 6, Fig. 3(d) is a photograph of Reference Example 7, and Fig. 3(e) is a photograph of Reference Example 8. Fig. 4 is photographs showing results of the observation of the metal structures of the TiAl alloys of Examples 2 to 4 and Reference Examples 9 and 10, that is, Fig. 4(a) is a photograph of Example 2, Fig. 4(b) is a photograph of Example 3, Fig. 4(c) is a photograph of Example 4, Fig. 4(d) is a photograph of Reference Example 9, and Fig. 4(e) is a photograph of Reference Example 10.

[0045] As shown in Figs. 3(a) to 3(c), in Reference Examples 4 to 6, a metal structure in which the solidification process was in the α single phase region (α solidification) was observed. On the other hand, as shown in Figs. 3(d) and 3(e), in Reference Examples 7 and 8, a metal structure in which the solidification process was in the γ single phase region (γ solidification) was observed. In the metal structure in which the solidification process was in the γ single phase region (γ solidification), columnar crystals were formed and the anisotropy was observed. As shown in Figs. 4(a) to 4(c), in Examples 2 to 4, a metal structure in which the solidification process was in the α single phase region (α solidification) was observed. On the other hand, as shown in Figs. 4(d) to 4(e), in Reference Examples 9 and 10, a metal structure in which the solidification process was in the γ single phase region (γ solidification) was observed. In the metal structure in which the solidification process was in the γ single phase region (γ solidification), columnar crystals were formed, and the anisotropy was observed. From this result, it was found that if the content of Al is more than 50 at%, the solidification process was in the γ single phase region (γ solidification), and the anisotropy occurs.

[0046] As shown in Figs. 4(a) to 4(c), the metal structures of Examples 2 to 4 were formed of fine crystal grains with a crystal grain size of 200 μm or less. The metal structures of Examples 2 to 4 were formed of lamellar grains and γ grains, and boride with a grain size of 0.1 μm or less was contained in the γ grains. In the metal structures of Examples 2 to 4, relative to a total of the volume fraction of the lamellar grain and the volume fraction of the γ grain being 100 volume %, a volume fraction of the lamellar grains is 80 volume % or more, and the balance is the γ grains. An area ratio of each grain was calculated by applying image processing to information on the contrast of each grain in the photographs of the metal structures, and the thus obtained area ratio was regarded as the volume fraction of each grain. In the metal structures of Examples 2 to 4, the segregation of Nb was not observed.

[0047] The hardness of the TiAl alloy before and after being subjected to the hot isostatic pressing process was evaluated. Vickers hardness of the TiAl alloys of Examples 2 to 4 and Reference Examples 4 to 10 was measured at room temperature. Vickers hardness was measured in accordance with ASTM E 92. Fig. 5 is a graph showing measurement results of Vickers hardness of the TiAl alloys before being subjected to the hot isostatic pressing process. Fig. 6 is a graph showing measurement results of Vickers hardness of the TiAl alloys subjected to the hot isostatic pressing process. In Figs. 5 and 6, a horizontal axis represents the content of Al of each TiAl alloy, a vertical axis represents Vickers hardness, Vickers hardness of the TiAl alloys of Examples 2 to 4 is indicated by white circles, and Vickers hardness of the TiAl alloys of Examples 4 to 10 is indicated by black circles.

[0048] Vickers hardness of the TiAl alloys of Examples 2 to 4 before and after being subjected to the hot isostatic pressing process was 200 HV or more. Further, if the content of Al of the TiAl alloy was in a range from 48 at% or more to 50 at% or less, Vickers hardness of Examples 2 to 4 was larger than Vickers hardness of Reference Examples 4 to 6. On the other hand, if the content of Al of the TiAl alloy was more than 50 at%, Vickers hardness of Reference Examples 7 and 8 was substantially the same as Vickers hardness of Reference Examples 9 and 10. From this result, it is considered that Nb contributes to the improvement of the mechanical strength, if the content of Al of the TiAl alloy is in a range from 48 at% or more to 50 at% or less.

[0049] The room temperature mechanical characteristics of the TiAl alloys were evaluated. Tensile tests were performed at room temperature for the TiAl alloys of Example 1 and Comparative Example 1. The tensile tests were performed in accordance with ASTM E8. Fig. 7 is a graph showing results of the tensile tests. Fig. 7 shows a stress-strain curve of each TiAl alloy, with a horizontal axis representing strain and a vertical axis representing stress. Example 1 had greater room temperature strength than Comparative Example 1. Further, the room temperature ductility of Example 1 was substantially the same as that of Comparative Example 1. More specifically, the room temperature ultimate tensile strength of Example 1 was 400 MPa or more, and the room temperature tensile fracture strain of Example 1 was 1.0 % or more.

[0050] The high temperature mechanical characteristics of the TiAl alloys were evaluated. Creep tests were performed at high temperature for the TiAl alloys of Example 1 and Comparative Example 1. The creep tests were performed in accordance with ASTM E 139. In a creep test condition, a test temperature was 800 °C and applied stress was 150 MPa. Fig. 8 is a graph showing results of the creep tests. Fig. 8 shows a creep curve of each TiAl alloy, with a horizontal axis representing a creep time and a vertical axis representing creep strain. The high temperature creep characteristics of Example 1 were four times or more higher than those of Comparative Example 1. As described above, Example 1 had more improved high temperature creep characteristic than Comparative Example 1. More specifically, the high temperature creep characteristics of Example 1 were such that the creep strain after the elapse of 200 hours was 2 % or less, when the tests were performed at a test temperature of 800 °C and applied stress of 150 MPa. The high temperature creep characteristics of Example 1 were such that the creep strain after the elapse of 400 hours was 7% or less when the tests were performed at the test temperature of 800 °C and the applied stress of 150 MPa.

[0051] As shown in Figs. 7 and 8, it was found that the TiAl alloy of Example 1 had excellent mechanical strength and ductility which were improved in a good balance. On the other hand, the TiAl alloy of Comparative Example 1 had more degraded room temperature strength and high temperature mechanical characteristics than the TiAl alloy of Example 1. The reason for the above degradation is considered to be due to the influence or the like of Cr contained in the TiAl alloy of Comparative Example 1.

[0052] The oxidation resistance of the TiAl alloys was evaluated. Oxidation tests were performed for the TiAl alloys of Example 1 and Comparative Example 1. The oxidation tests were performed by continuous oxidization at a temperature of 750 °C for a hour of 200 hours in air atmosphere. After performing the oxidation tests, the observation of cross-sectional areas was performed to evaluate the thickness of oxide layers. Fig. 9 is photographs showing results of the observation of the cross-sectional areas after performing the oxidation tests, that is, Fig. 9(a) is a photograph of Example 1, and Fig. 9(b) is a photograph of Comparative Example 1. The thickness of the oxide layer of Example 1 was 2.8 μm. The thickness of the oxide layer of Comparative Example 1 was 4.3 μm. From this result, it was found that Example 1 had more excellent oxidation resistance than Comparative Example 1.

[Industrial Applicability]

[0053] The present disclosure can improve the mechanical strength and the ductility of a TiAl alloy in a good balance, and thus, is useful for turbine blades and the like of aircraft engine components.

Claims

1. A TiAl alloy, comprising:

    48 at% or more and 50 at% or less of Al;
    3 at% or more and 5 at% or less of Nb;
    0.1 at% or more and 0.3 at% or less of B; and
    the balance being Ti and inevitable impurities.

2. The TiAl alloy according to claim 1, wherein a content of Al is 49 at%.

3. The TiAl alloy according to claim 1 or 2, wherein a metal structure is formed of a lamellar grain and a γ grains, and is free of a segregation of Nb.

4. The TiAl alloy according to claim 3, wherein a volume fraction of the lamellar grain is 80 volume % or more, relative to a total of the volume fraction of the lamellar grain and the volume fraction of the γ grain being 100 volume %.

5. The TiAl alloy according to any one of claims 1 to 4, wherein Vickers hardness at a room temperature is 200 HV or more.

6. The TiAl alloy according to any one of claims 1 to 5, wherein room temperature ultimate tensile strength is 400 MPa or more and room temperature tensile fracture strain is 1.0 % or more.

7. The TiAl alloy according to any one of claims 1 to 6, wherein creep strain after an elapse of 200 hours is 2 % or less, when a temperature is 800 °C and applied stress is 150 MPa.

8. A method of manufacturing a TiAl alloy, comprising: a casting step of casting a TiAl alloy raw material which contains 48 at% or more and 50 at% or less of Al, 3 at% or more and 5 at% or less of Nb, 0.1 at% or more and 0.3 at% or less of B, and the balance being Ti and inevitable impurities.

9. The method of manufacturing the TiAl alloy according to claim 8, wherein in the casting step, a solidification process passes through an α single phase region.

10. The method of manufacturing the TiAl alloy according to claim 8 or 9, comprising: a hot isostatic pressing process step for performing a hot isostatic pressing process of applying hot isostatic pressing to the cast TiAl alloy at a temperature range from 1250 °C or higher to 1350 °C or lower, for a hour range from 1 hour or more to 5 hours or less, at an applied stress range from 158 MPa or higher to 186 MPa or lower, and then furnace cooling the cast TiAl alloy subjected to the hot isostatic pressing to 900 °C, followed by rapid cooling of the cast TiAl alloy subjected to the hot isostatic pressing from 900 °C.

11. The method of manufacturing the TiAl alloy according to claim 10, comprising: a stress relieving step of relieving stress by holding the TiAl alloy subjected to the hot isostatic pressing process at a temperature range from 800 °C or higher to 950 °C or lower for a hour range from 1 hour or more to 5 hours or less.

FIG. 1

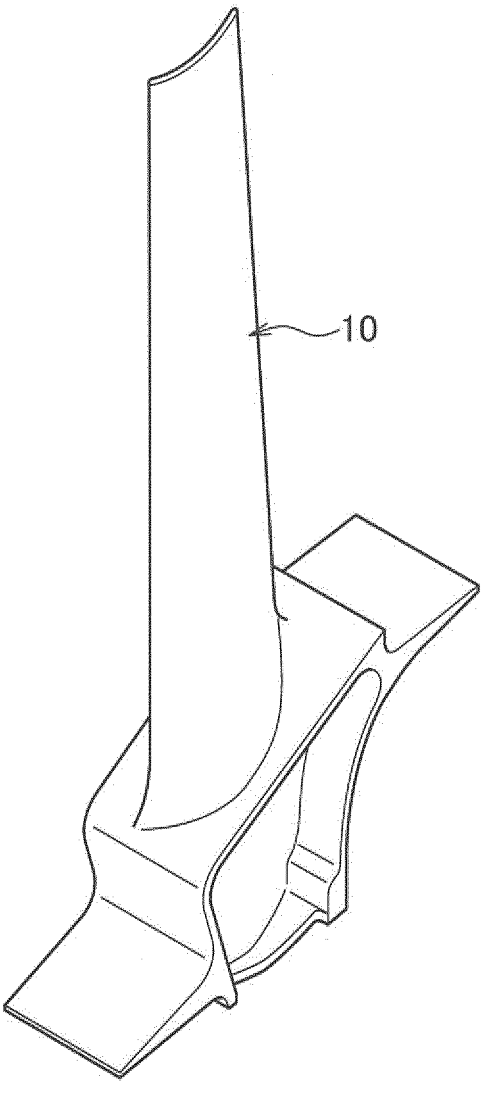


FIG. 2

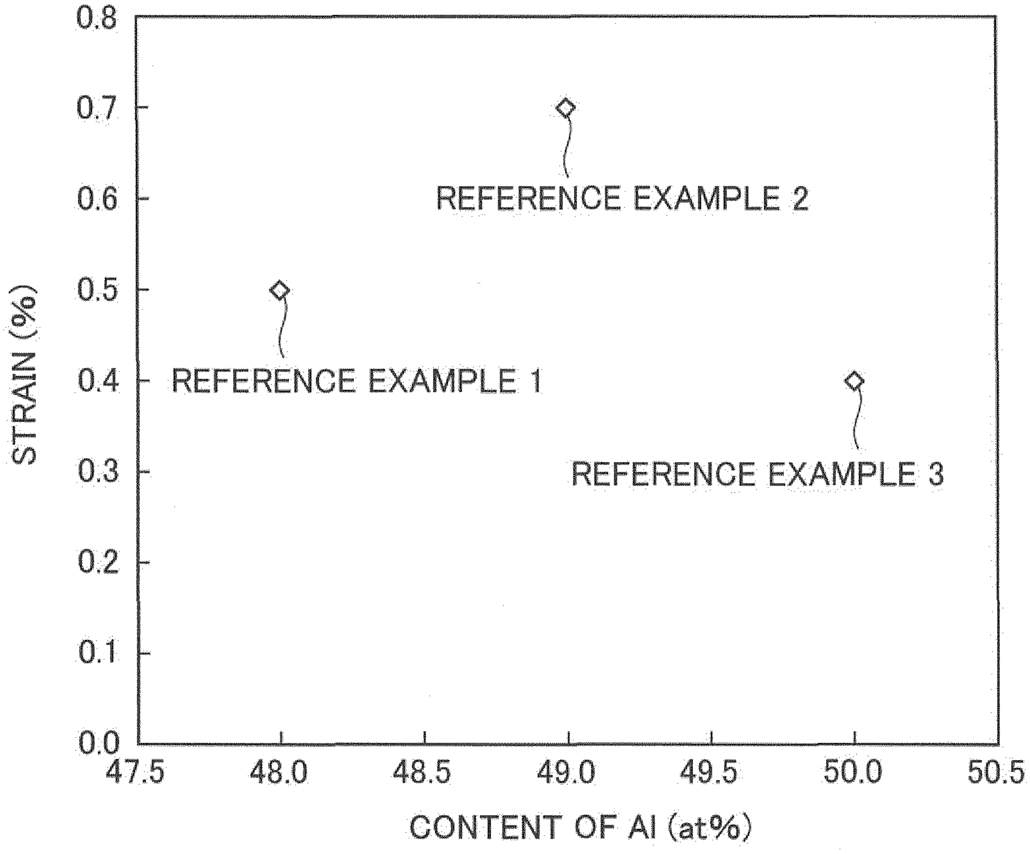

0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
STRAIN (%)
47.5
48.0
48.5
49.0
49.5
50.0
50.5
CONTENT OF Al (at%)
REFERENCE EXAMPLE 1
REFERENCE EXAMPLE 2
REFERENCE EXAMPLE 3

FIG. 3

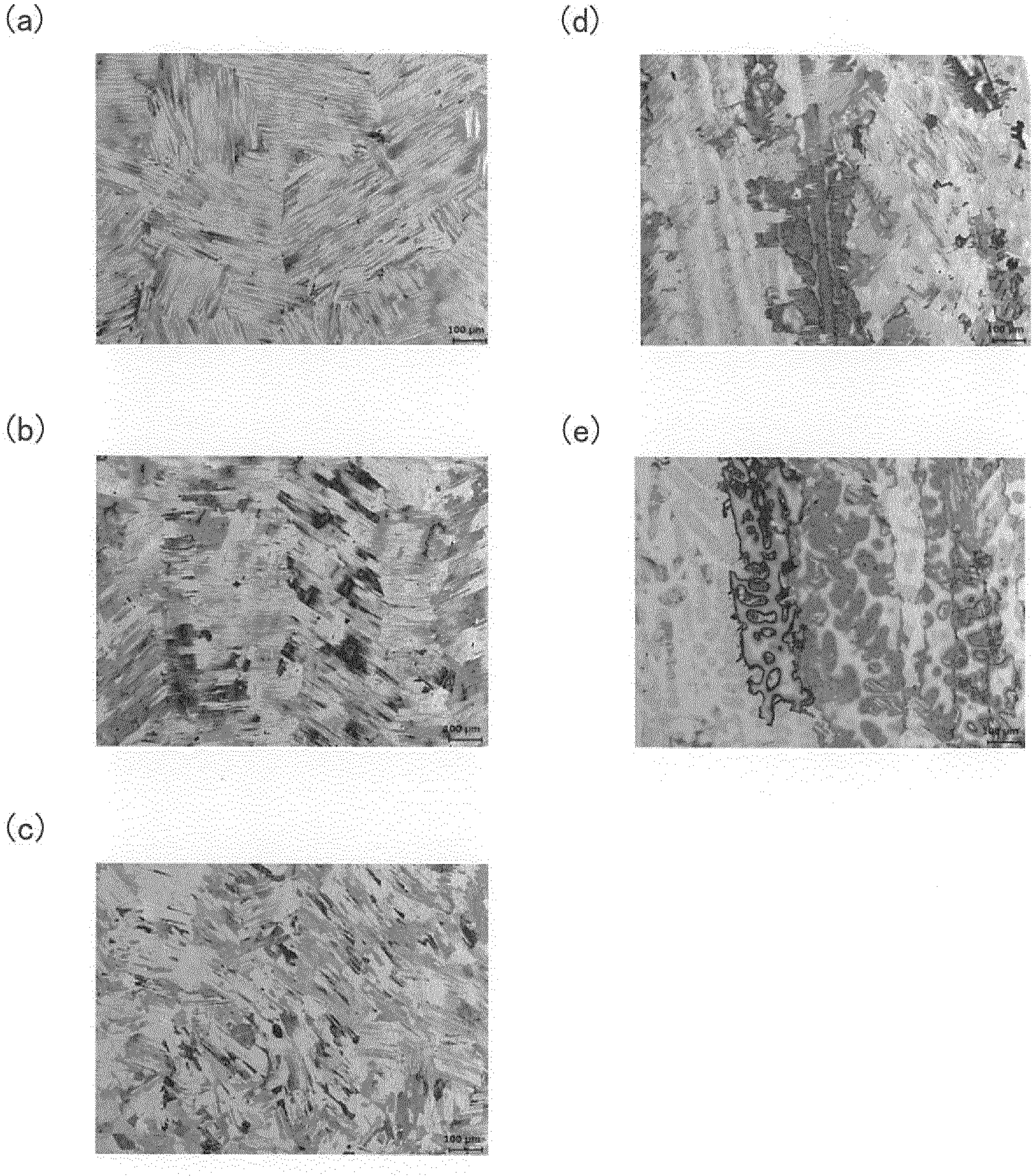


FIG. 4

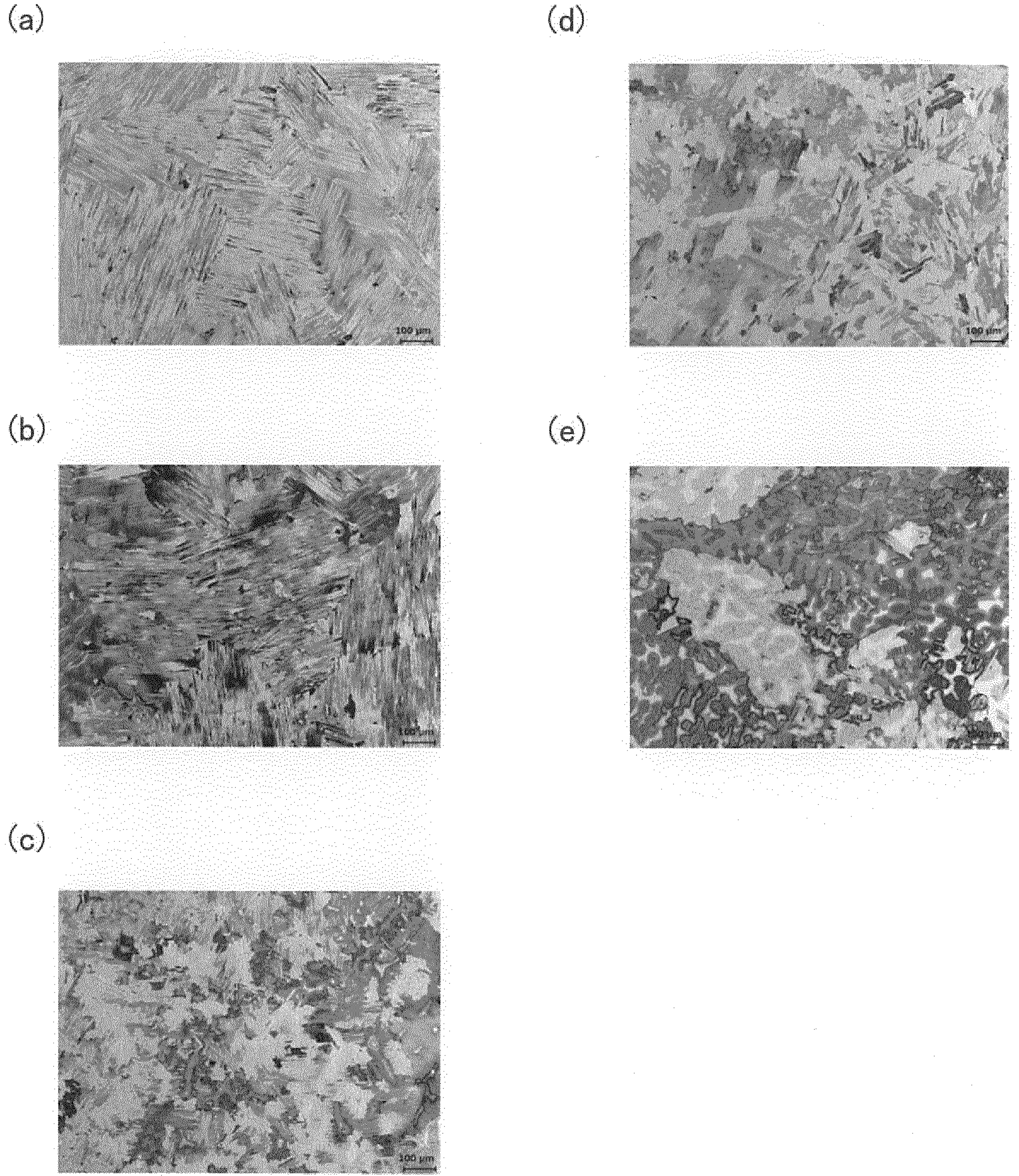


FIG. 5

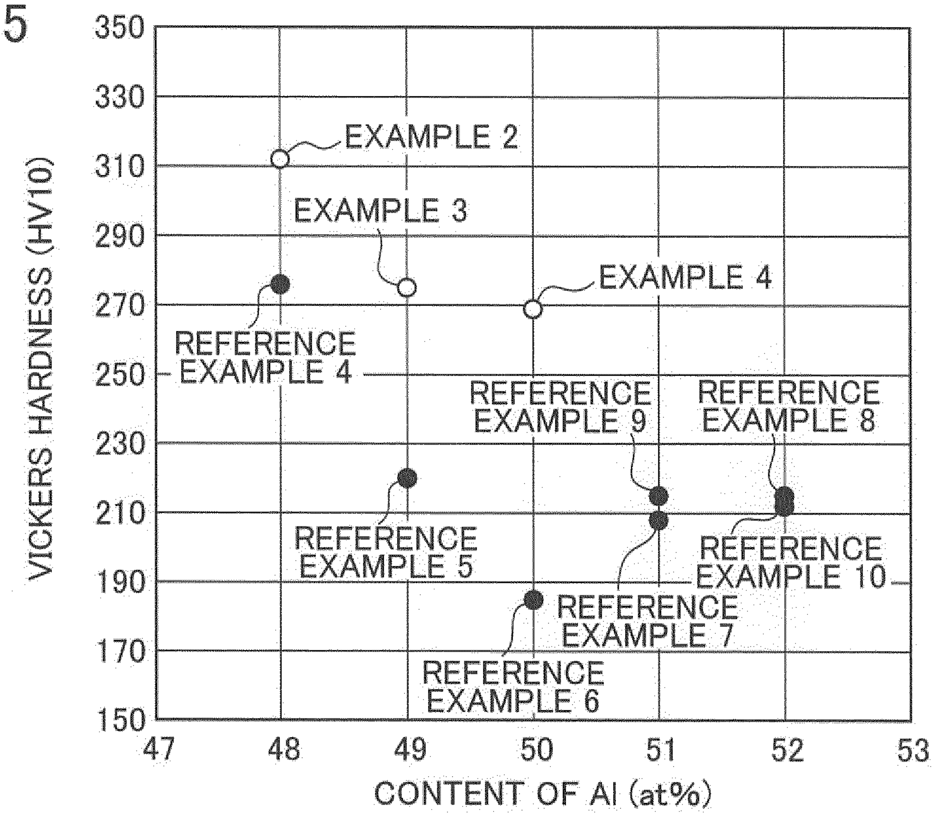

350
330
310
290
270
250
230
210
190
170
150
47
48
49
50
51
52
53
VICKERS HARDNESS (HV10)
CONTENT OF Al (at%)
EXAMPLE 2
EXAMPLE 3
EXAMPLE 4
REFERENCE EXAMPLE 4
REFERENCE EXAMPLE 9
REFERENCE EXAMPLE 8
REFERENCE EXAMPLE 5
REFERENCE EXAMPLE 10
REFERENCE EXAMPLE 7
REFERENCE EXAMPLE 6

FIG. 6

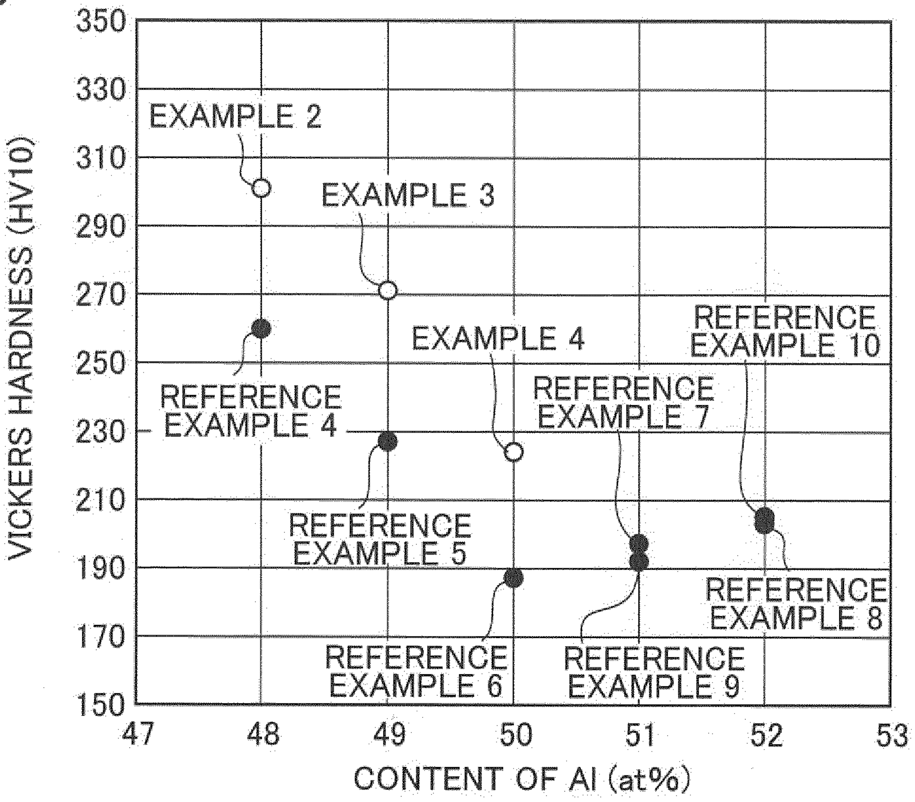

350
330
310
290
270
250
230
210
190
170
150
47
48
49
50
51
52
53
VICKERS HARDNESS (HV10)
CONTENT OF Al (at%)
EXAMPLE 2
EXAMPLE 3
EXAMPLE 4
REFERENCE EXAMPLE 10
REFERENCE EXAMPLE 4
REFERENCE EXAMPLE 7
REFERENCE EXAMPLE 5
REFERENCE EXAMPLE 8
REFERENCE EXAMPLE 6
REFERENCE EXAMPLE 9

FIG. 7

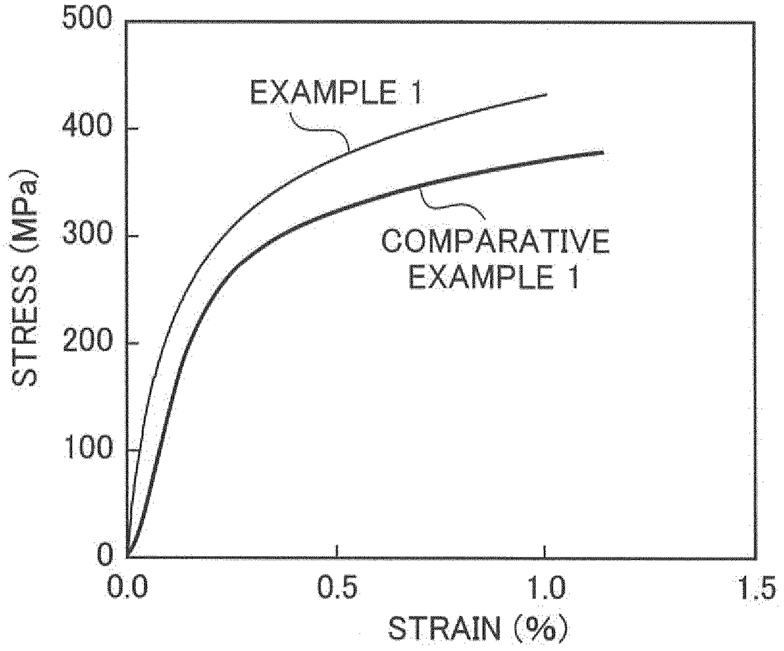

500
400
300
200
100
0
STRESS (MPa)
EXAMPLE 1
COMPARATIVE
EXAMPLE 1
0.0
0.5
1.0
1.5
STRAIN (%)

FIG. 8

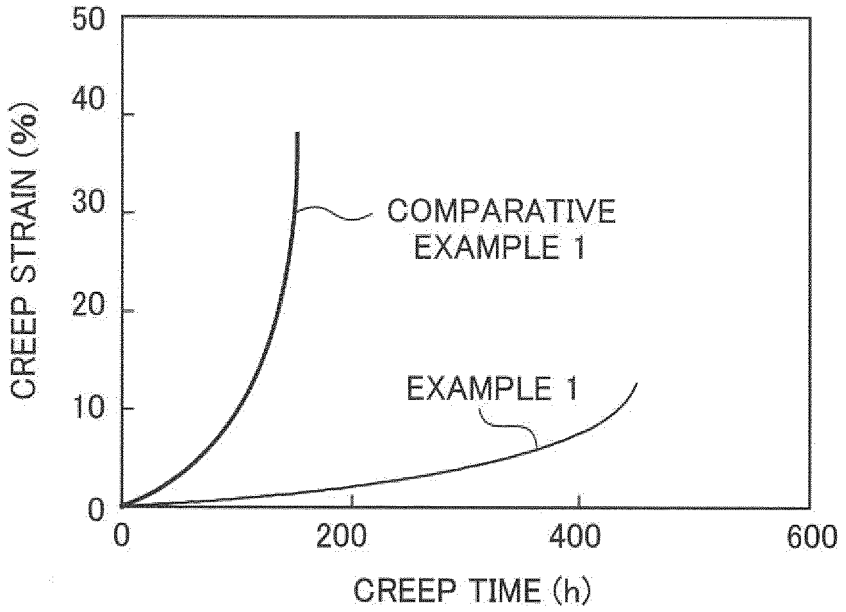
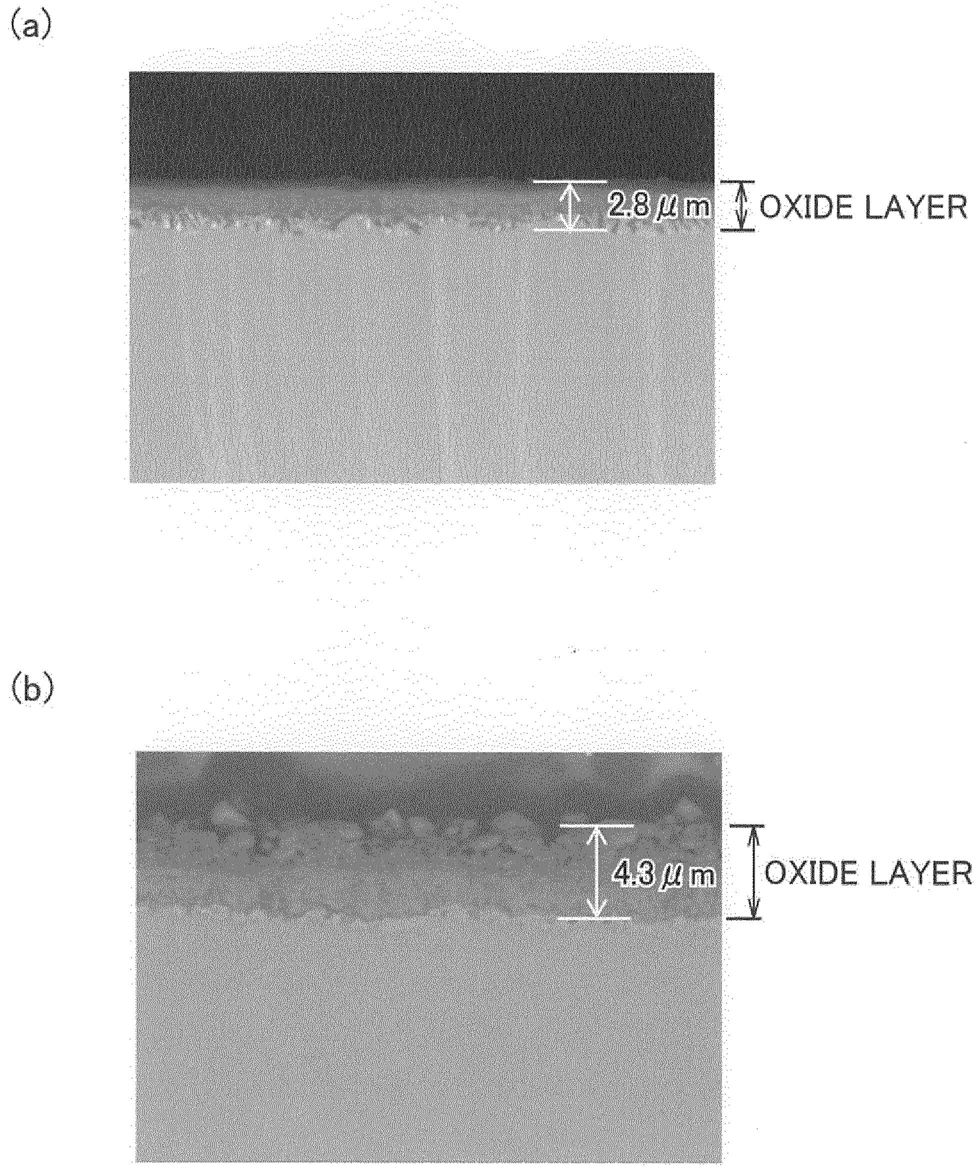

50
40
30
20
10
0
CREEP STRAIN (%)
COMPARATIVE
EXAMPLE 1
EXAMPLE 1
0
200
400
600
CREEP TIME (h)

FIG. 9



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2020/011936

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. B21J5/00(2006.01)i, C22C14/00(2006.01)i, C22F1/00(2006.01)n, C22F1/18(2006.01)i

FI: C22C14/00Z, C22F1/18H, B21J5/00G, C22F1/00630K, C22F1/00630C, C22F1/00650A, C22F1/00651B, C22F1/00640B, C22F1/00694B, C22F1/00694Z, C22F1/00611, C22F1/00630A, C22F1/00691B, C22F1/00691C, C22F1/00692A, C22F1/00692B

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. B21J5/00, C22C14/00, C22F1/00, C22F1/18

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

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2020
Registered utility model specifications of Japan	1996-2020
Published registered utility model applications of Japan	1994-2020

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 1-298127 A (SUMITOMO METAL INDUSTRIES, LTD.) 01.12.1989 (1989-12-01)	1-11
A	JP 5-230568 A (ASEA BROWN BOVERI AG) 07.09.1993 (1993-09-07)	1-11
A	JP 2008-520826 A (GKSS-FORSCHUNGSZENTRUM GEESTHACHT GMBH) 19.06.2008 (2008-06-19)	1-11
A	JP 8-294783 A (NHK SPRING CO., LTD.) 12.11.1996 (1996-11-12)	1-11
A	JP 6-49569 A (SUMITOMO LIGHT METAL IND LTD.) 22.02.1994 (1994-02-22)	1-11

☐ 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
09.06.2020

Date of mailing of the international search report
23.06.2020

Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2020/011936

JP 1-298127 A	01.12.1989	(Family: none)
JP 5-230568 A	07.09.1993	US 5286443 A US 5342577 A US 5207982 A EP 455005 A1 RU 1839683 C AT 127860 T
JP 2008-520826 A	19.06.2008	US 2010/0015005 A1 WO 2006/056248 A1 EP 1819838 A1 CA 2587237 A1 KR 10-2007-0086597 A CN 101056998 A AT 425272 T ES 2322082 T3 RU 2007123588 A
JP 8-294783 A	12.11.1996	US 5863670 A
JP 6-49569 A	22.02.1994	(Family: none)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2013209750 A **[0003]**