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

(11) EP 4 502 200 A1

(12) EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
05.02.2025 Bulletin 2025/06

(21) Application number: **23775007.0**

(22) Date of filing: **23.03.2023**

(51) International Patent Classification (IPC):
***C22C 1/02** (2006.01)* ***B22D 21/04** (2006.01)*
***B22D 23/00** (2006.01)* ***C22B 7/00** (2006.01)*
***C22B 9/10** (2006.01)* ***C22C 14/00** (2006.01)*

(52) Cooperative Patent Classification (CPC):
B22D 21/04; B22D 23/00; C22B 7/00; C22B 9/10; C22C 1/02; C22C 14/00

(86) International application number:
PCT/JP2023/011444

(87) International publication number:
WO 2023/182413 (28.09.2023 Gazette 2023/39)

(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 ME MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

(30) Priority: **25.03.2022 JP 2022050457**

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(54) METHOD FOR MANUFACTURING TIAL ALLOY CASTING MATERIAL, TIAL ALLOY CASTING MATERIAL, MOVING BLADE FOR JET ENGINE, AND TURBINE WHEEL

(57) A method for manufacturing a TiAl alloy casting material includes a melting step of melting a raw material including Ti and Al to prepare a molten metal; a deoxidation material adding step of adding a deoxidation material including Ca to either or both of the raw material and the molten metal, the deoxidation material being added such that the Ca concentration in the total mass of the raw material and the deoxidation material is 0.2 mass% to 1.0 mass%; and a deoxidation step of heating the molten metal including the deoxidation material for maintaining a molten state to generate a fume including a reaction product of oxygen and Ca in the molten metal, so that the oxygen in the molten metal is removed.

Processed by Luminess, 75001 PARIS (FR)

Description

TECHNICAL FIELD

[0001] The present invention relates to a method for manufacturing a TiAl alloy casting material, a TiAl alloy casting material, a turbine blade for a jet engine, and a turbine wheel.

[0002] Priority is claimed from Japanese Patent Application No. 2022-050457, filed March 25, 2022, the content of which is incorporated herein by reference.

BACKGROUND ART

[0003] In the related art, Ni-based superalloys have been used as materials for turbine blades for jet engines, turbocharger turbine wheels for passenger cars, and the like. In recent years, TiAl alloys have been attracting attention as new materials used for these members. The density of the TiAl alloys is approximately 1/2 of the density of the Ni-based superalloys. For this reason, even though the members are large, the weight thereof is small, which greatly contributes to the improvement of engine efficiency and reduction of fuel consumption and carbon dioxide emission through weight reduction.

[0004] In members made of the TiAl alloys, which have been put into practical use as turbine blades for jet engines and turbine wheels, the concentration of impurities in the TiAl alloys forming the members is naturally specified. Regarding oxygen, which is most likely to be mixed as an impurity, the oxygen content in the TiAl alloy is specified to be, for example, 0.12 mass% or less. In a case in which the oxygen content in the TiAl alloys exceeds 0.12 mass%, problems are likely to occur such that the impact resistance characteristics of the members made of the TiAl alloys deteriorate and damage of the members occurs during use.

[0005] In general, TiAl alloy casting materials manufactured by casting methods are used for the turbine blades for jet engines and the turbine wheels made of TiAl alloys. As raw materials used for the casting, metal element raw materials such as sponge titanium and Al granules, and/or mother alloy ingots (casting blocks) made using these metal element raw materials are used.

[0006] At present, in the case where the TiAl alloy casting materials to be turbine blades for jet engines and turbine wheels are cast, manufacturing methods shown below are used to obtain products having a sufficiently low oxygen content satisfying the component specifications of the TiAl alloys. That is, the method for melting a raw material in a vacuum atmosphere or in an inert gas atmosphere by using a vacuum melting furnace prevents oxygen from being mixed in the molten raw material from the atmosphere. Moreover, the method for melting the raw material in a water-cooled copper crucible prevents oxygen from being mixed in the molten metal.

[0007] In the case where metal materials such as iron-based or Ni-based alloys are melted, oxide ceramic crucibles are generally used. However, since the TiAl alloys have an active molten metal, in the case where a TiAl alloy is melted in an oxide ceramic crucible, oxygen is mixed in the molten metal from the crucible, and the oxygen concentration in the casting material increases.

[0008] In addition, in the case where the TiAl alloy casting materials to be turbine blades for jet engines and turbine wheels are cast, raw materials having a low oxygen content are used to obtain products having a sufficiently low oxygen content that satisfies the component specifications of the TiAl alloys. Specifically, metal element raw materials having a low oxygen content and/or mother alloy ingots (casting blocks) having a low oxygen content, which are formed of the metal element raw materials having a low oxygen content, are used.

[0009] The mother alloy ingots having a low oxygen content are usually manufactured by a casting method shown below. That is, a method for melting a raw material, which is a mother alloy ingot, in a water-cooled copper crucible installed in a vacuum melting furnace under a vacuum atmosphere or an inert gas atmosphere is used.

[0010] Patent Document 1 describes a method for manufacturing a TiAl alloy ingot by casting, into a mold, a molten metal obtained by melting Ti and Al, which are a molten raw material, in a ceramic crucible by high-frequency induction melting. In addition, Patent Document 1 discloses that, by using yttria (Y_2O_3), which is the most chemically stable compound, as a material for the ceramic crucible, the amount of oxygen generated by the decomposition of the ceramic crucible during the melting can be suppressed, and the concentration of oxygen mixed in the TiAl alloy can be suppressed.

[0011] Patent Document 2 discloses a method for manufacturing a casting block of a TiAl-based alloy, in which, in an alloy raw material, the oxygen content of a Ti raw material is 800 ppm or less, the oxygen content of an Al raw material is 100 ppm or less, the oxygen content of the other alloy components is 2000 ppm or less in the case where the other alloy components are Cr, V, or Nb, and the oxygen content of the other alloy components is 3000 ppm or less in the case where the other alloy components are Mn. Patent Document 2 describes that a molten base material, which is made of a primary casting block that is component-adjusted in advance by melting and solidifying the alloy raw material, is melted in a crucible made of water-cooled copper. In addition, Patent Document 2 describes that the alloy material is stored in an inert gas atmosphere so as not to be affected by surface oxidation or the like.

[0012] Patent Document 3 describes a method for manufacturing high-purity TiAl-based intermetallic compound, in which a high-purity Ti having an oxygen content of 200 ppm or less and high-purity Al having a purity of 99.99 weight% or more are used as a base material, the base material is melted and cast with the oxygen content reduced to 0.03% or less, and then the cast material is annealed. Patent Document 3 describes that the melting and solidification are repeated on a copper hearth multiple times.

[0013] Patent Document 4 describes a method for melting a raw material made of 48 to 70 at% of titanium and 30 to 52 at% of aluminum in a calcia crucible to produce a TiAl intermetallic compound alloy. In addition, Patent Document 4 describes that a titanium raw material is heated in vacuum in advance to perform a degassing treatment, and then the titanium raw material and an aluminum raw material are charged into the crucible and melted by a vacuum induction melting method.

[0014] Non Patent Document 1 describes that deoxidation is performed by inductively melting a Ti alloy in a water-cooled copper crucible and adding a Ca alloy thereto. In addition, Non Patent Document 1 describes that the analysis of an ingot obtained by deoxidizing a TiAl mother alloy containing 0.16 mass% of oxygen by using an AlCa alloy as a deoxidation material showed that the ingot is deoxidized to O = 0.02% at Ca ≥ 0.3%.

CITATION LIST

PATENT DOCUMENTS

[0015]

Patent Document 1: Japanese Unexamined Patent Application, First Publication No. 2011-36877

Patent document 2: Japanese Unexamined Patent Application, First Publication No. 2009-113060

Patent Document 3: Japanese Unexamined Patent Application, First Publication No. H3-193839

Patent Document 4: Japanese Unexamined Patent Application, First Publication No. H3-199330A

NON PATENT DOCUMENT

[0016] Non Patent Document 1: Tomoki Shibata, Noboru Demizu, Deoxidation of TiAl, Electric Steelmaking, Vol. 64, February 1993, No. 1, p. 32 to 39

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0017] In the related art, in the case where the TiAl alloy casting materials having a sufficiently low oxygen content are manufactured, it is necessary to use methods using special devices that melt a raw material by using a water-cooled copper crucible installed in a vacuum melting furnace under a vacuum atmosphere or an inert gas atmosphere and/or methods using special raw materials having a low oxygen content. For this reason, there is a demand for increasing the number of options of the devices and the raw materials that can be used in the case where the TiAl alloy casting materials having a sufficiently low oxygen content are manufactured.

[0018] The present invention has been made in view of the above circumstances, and an object of the present invention is to provide a method for manufacturing a TiAl alloy casting material, which is capable of obtaining a TiAl alloy casting material having a sufficiently low oxygen content, and has high versatility in that various devices and raw materials can be used, a TiAl alloy casting material of which the oxygen content is 0.12 mass% or less, and a turbine blade for a jet engine and a turbine wheel, which are made of the TiAl alloy casting material of which the oxygen content is 0.12 mass% or less.

SOLUTION TO PROBLEM

[0019]

[1] A method for manufacturing a TiAl alloy casting material, the method including a melting step of melting a raw material including Ti and Al to prepare a molten metal; a deoxidation material adding step of adding a deoxidation material including Ca to either or both of the raw material and the molten metal, the deoxidation material being added such that the Ca concentration in the total mass of the raw material and the deoxidation material is 0.2 mass% to 1.0

mass%; and a deoxidation step of heating the molten metal including the deoxidation material for maintaining a molten state to generate a fume including a reaction product of oxygen and Ca in the molten metal, so that the oxygen in the molten metal is removed.

[2] The method for manufacturing the TiAl alloy casting material according to [1], in which the deoxidation material is an AlCa alloy.

[3] The method for manufacturing a TiAl alloy casting material according to [1] or [2], in which the melting step is a step of melting the raw material in an oxide ceramic crucible; the deoxidation material adding step is either or both of a step of putting the deoxidation material into the oxide ceramic crucible together with the raw material and a step of adding the deoxidation material to the molten metal put into the oxide ceramic crucible; and, in the deoxidation step, the molten metal including the deoxidation material put into the oxide ceramic crucible is heated and melted.

[4] The method for manufacturing a TiAl alloy casting material according to [1] or [2], in which the deoxidation material adding step is a step of putting the deoxidation material into an oxide ceramic crucible installed in a vacuum melting furnace together with the raw material; the melting step is a step of melting the raw material in the oxide ceramic crucible installed in the vacuum melting furnace under an Ar atmosphere after the deoxidation material adding step; and, in the deoxidation step, the molten metal including the deoxidation material is heated and melted in the oxide ceramic crucible installed in the vacuum melting furnace under the Ar atmosphere.

[5] The method for manufacturing a TiAl alloy casting material according to [3], in which the oxide ceramic crucible is installed in an atmospheric melting furnace under an air atmosphere; the melting step includes a mold installation step of installing the wider opening portion of a funnel-shaped mold toward the oxide ceramic crucible to cover the opening portion of the oxide ceramic crucible; an atmosphere replacement step of supplying an Ar gas into the oxide ceramic crucible; and a heating step of heating the oxide ceramic crucible; the deoxidation material adding step is either or both of a step of putting the deoxidation material into the oxide ceramic crucible together with the raw material, and a step of adding the deoxidation material to the molten metal put into the oxide ceramic crucible via the funnel-shaped mold; in the deoxidation step, the molten metal including the deoxidation material is heated and melted in the oxide ceramic crucible of which the opening portion is covered with the funnel-shaped mold, the fume in the oxide ceramic crucible is discharged via the funnel-shaped mold; and, after the deoxidation step, a casting step of turning the atmospheric melting furnace upside down in a state in which the oxide ceramic crucible and the funnel-shaped mold are integrated with each other, to pour the molten metal into the funnel-shaped mold from the oxide ceramic crucible and cool the molten metal is performed.

[6] The method for manufacturing a TiAl alloy casting material according to any one of [1] to [5], in which the raw material includes either or both of TiAl alloy cutting chips and TiAl alloy casting scraps.

[7] A TiAl alloy casting material containing 0.04 mass% to 0.10 mass% of oxygen and 0.01 mass% to 0.03 mass% of Ca.

[8] A TiAl alloy casting material containing 31.9 mass% to 34.2 mass% of Al, 4.0 mass% to 5.4 mass% of Nb, 2.3 mass% to 3.0 mass% of Cr, 0.04 mass% to 0.12 mass% of oxygen, and 0.01 mass% to 0.07 mass% of Ca, with the balance being Ti and impurities.

[9] A turbine blade for a jet engine made of the TiAl alloy casting material according to [7] or [8].

[10] A turbine wheel made of the TiAl alloy casting material according to [7] or [8].

ADVANTAGEOUS EFFECTS OF INVENTION

[0020] The method for manufacturing a TiAl alloy casting material according to the present invention includes the melting step of melting the raw material including Ti and Al to prepare the molten metal; the deoxidation material adding step of adding the deoxidation material including Ca to either or both of the raw material and the molten metal, the deoxidation material being added such that the Ca concentration in the total mass of the raw material and the deoxidation material is 0.2 mass% to 1.0 mass%; and the deoxidation step of heating the molten metal including the deoxidation material to maintain the molten state to generate the fume including the reaction product of oxygen and Ca in the molten metal, so that the oxygen in the molten metal is removed. For this reason, by pouring the molten metal after the deoxidation step into the mold and cooling the molten metal, the TiAl alloy casting material having a sufficiently low oxygen content is obtained.

[0021] Accordingly, according to the method for manufacturing the TiAl alloy casting material according to the present invention, the TiAl alloy casting material having a sufficiently low oxygen content can be obtained without using a special device or using a special raw material having a low oxygen content, and various devices and raw materials can be used. For example, even in a case where the raw material contains a defective raw material having a large amount of oxygen or in a case where the molten metal contains oxygen mixed from the oxide ceramic crucible and/or the atmosphere, by using the method for manufacturing a TiAl alloy casting material according to the present invention, a TiAl alloy casting material having a sufficiently low oxygen content is obtained.

BRIEF DESCRIPTION OF DRAWINGS

[0022]

FIG. 1 is a process diagram for showing an example of a method for manufacturing a TiAl alloy casting material according to the present embodiment.

FIG. 2 is a process diagram for showing an example of the method for manufacturing the TiAl alloy casting material according to the present embodiment.

FIG. 3 is a process diagram for showing an example of the method for manufacturing the TiAl alloy casting material according to the present embodiment.

FIG. 4 is a process diagram for showing an example of the method for manufacturing the TiAl alloy casting material according to the present embodiment.

FIG. 5 is a process diagram for showing an example of the method for manufacturing the TiAl alloy casting material according to the present embodiment.

FIG. 6 is a process diagram for showing an example of the method for manufacturing the TiAl alloy casting material according to the present embodiment.

FIG. 7 is a process diagram for showing an example of the method for manufacturing the TiAl alloy casting material according to the present embodiment.

DESCRIPTION OF EMBODIMENTS

[0023] In order to solve the above-described problems, the present inventors have conducted intensive studies as shown below.

[0024] That is, in a case where a special device for melting a raw material using a water-cooled copper crucible installed in a vacuum melting furnace in a vacuum atmosphere or an inert gas atmosphere is used to obtain a TiAl alloy casting material having a sufficiently low oxygen content, the initial amount of facility investment and operating costs are high. Moreover, since a water-cooled copper crucible is used, the amount of molten metal that can be melted is small, the number of casting materials that can be cast in one batch is small, and the productivity is insufficient. In addition, in the case where the water-cooled copper crucible is used, since the overheating temperature of the molten metal is low, defectiveness casting around the molten metal is likely to occur during casting, and the yield of good products is likely to be low.

[0025] In order to solve the problems in the case where a water-cooled copper crucible is used, it is considered to use an oxide ceramic crucible that is generally used in a case where a metal material such as an iron-based or Ni-based alloy is melted, instead of the water-cooled copper crucible. In the case where the oxide ceramic crucible is used, compared to the case where the water-cooled copper crucible is used, the amount of the molten metal that can be melted can be increased, and the overheating temperature of the molten metal can also be increased.

[0026] However, the molten metal of the TiAl alloy is very active. For this reason, in a case where a raw material containing Ti and Al is melted in the oxide ceramic crucible, oxygen derived from the material of the oxide ceramic crucible is mixed in the molten raw material. As a result, the TiAl alloy casting material obtained after casting has a large oxygen content. For this reason, in the related art, in the case where a TiAl alloy casting material having a sufficiently low oxygen content is manufactured, the oxide ceramic crucible could not be used.

[0027] In addition, in order to reduce the amount of initial facility investment and the operating costs, it is considered to use an atmospheric melting furnace instead of the vacuum melting furnace. However, in the case where the atmospheric melting furnace is used, oxygen in the air is mixed in the molten raw material. As a result, the TiAl alloy casting material obtained after casting has a large oxygen content.

[0028] In addition, in the case where a special raw material having a low oxygen content is used to obtain the TiAl alloy casting material having a sufficiently low oxygen content, the raw material is expensive, and a special device is required for storing the raw material. In addition, in the case where a mother alloy ingot having a low oxygen content is manufactured as the raw material having a low oxygen content, it is necessary to use a special device for melting the raw material using the water-cooled copper crucible installed in the vacuum melting furnace under a vacuum atmosphere or an inert gas atmosphere.

[0029] Meanwhile, it is required to use TiAl alloy scraps as a raw material of the TiAl alloy casting material. As the TiAl alloy scraps, TiAl alloy cutting chips and/or TiAl alloy casting scraps can be used. Examples of the TiAl alloy cutting chips include cutting chips generated in a case where a member such as a turbine blade for a jet engine is manufactured from the TiAl alloy casting material. In addition, examples of the TiAl alloy casting scraps include casting scraps made of parts that do not become a product of the TiAl alloy casting material, such as a runner generated in the case where precision casting of a TiAl alloy using lost wax casting is performed.

[0030] However, the TiAl alloy scrap has a high oxygen content. Specifically, an organic substance such as a coolant and a cutting oil adheres to the TiAl alloy cutting chips. Since the organic substance firmly adheres to the TiAl alloy cutting chips, it is difficult to sufficiently reduce the oxygen content even in a case where the TiAl alloy cutting chips are washed using an organic solvent or the like. In addition, the TiAl alloy casting scraps usually contain oxygen mixed by a reaction between a mold made of an oxide ceramic and a molten raw material. For this reason, the TiAl alloy casting scraps also have a high oxygen content. From these facts, in the related art, it is difficult to manufacture a TiAl alloy casting material having a sufficiently low oxygen content by using the raw material including the TiAl alloy scrap.

[0031] In recent years, the production amount of a member made of a TiAl alloy has rapidly expanded. In particular, the use of a turbine blade for a jet engine made of the TiAl alloy has been expanded worldwide, and the production amount thereof has been increased. However, the cost of a turbine blade for a jet engine made of the current TiAl alloy is several times that of a turbine blade for a jet engine made of a Ni-based superalloy. From this, there is a strong demand for reducing the cost of the TiAl alloy casting material that is used as a turbine blade for a jet engine.

[0032] Therefore, the present inventors have focused on deoxidation materials for molten raw materials and have conducted extensive research to solve the above problems and to realize a general-purpose method for manufacturing a TiAl alloy casting material in which a TiAl alloy casting material having a sufficiently low oxygen content is obtained, not only in a case where a special device that melts a raw material by using a water-cooled copper crucible installed in a vacuum melting furnace under a vacuum atmosphere or an inert gas atmosphere is used, but even also in a case where various devices, such as a device equipped with an oxide ceramic crucible installed in an atmospheric melting furnace or a vacuum melting furnace, and various raw materials, such as the TiAl alloy scrap, are used.

[0033] As a result, the present inventors have found that it is only required to add the deoxidation material to either or both of the raw material and the molten metal such that the Ca concentration in the total mass of the raw material and the deoxidation material including Ca is 0.2 mass% to 1.0 mass%, and then to heat the molten metal including the deoxidation material for maintaining a molten state. Ca is an element that is more likely to be bonded with oxygen than Ti and Al. For this reason, by heating the molten metal for maintaining a molten state, the Ca in the molten metal reacts with the oxygen in the molten metal to generate reaction products such as CaO, $CaTiO_3$, and $CaAl_2O_4$. These reaction products are discharged from the molten metal as fume (vapor). As a result, oxygen in the molten metal is removed together with Ca.

[0034] Moreover, the present inventors have confirmed that, by adding the deoxidation material including Ca such that the Ca concentration in the total mass of the raw material and the deoxidation material is within the above-described range, a TiAl alloy casting material having a sufficiently low oxygen content and having excellent impact resistance characteristics can be obtained without using a special device or using a special raw material having a low oxygen concentration, and have conceived the present invention.

[0035] Specifically, by using a method for adding the deoxidation material including Ca such that the above-described concentration is obtained, as shown in Examples described below, a TiAl alloy casting material having a sufficiently low oxygen content is obtained even in a case where a general-purpose melting furnace and an oxide ceramic crucible generally used in a case where a metal material is melted is used, or in a case where a raw material containing TiAl alloy scrap having a high oxygen concentration is used.

[0036] Hereinafter, a method for manufacturing a TiAl alloy casting material, a TiAl alloy casting material, a turbine blade for a jet engine, and a turbine wheel according to the present invention will be described in detail with reference to the accompanying drawings. The present invention is not limited to embodiments shown below.

[Method for manufacturing TiAl alloy casting material]

[0037] In the present embodiment, as an example of the method for manufacturing the TiAl alloy casting material, a case will be described in which a device including an oxide ceramic crucible 2 installed in an atmospheric melting furnace 1 is used.

[0038] FIGS. 1 to 7 are process diagrams for showing an example of the method for manufacturing the TiAl alloy casting material according to the present embodiment. In FIGS. 1 to 6, reference numeral 1 represents an atmospheric melting furnace, and reference numeral 2 represents an oxide ceramic crucible.

[0039] As the atmospheric melting furnace 1, a known atmospheric melting furnace can be used. In the present embodiment, the atmospheric melting furnace 1 is of a roll-over furnace type. As shown in FIG. 1, the atmospheric melting furnace 1 includes a substantially cylindrical accommodating section 1a that is open at the top. The atmospheric melting furnace 1 includes a furnace wall 1b and a high-frequency coil 4 that is installed in the furnace wall 1b and that heats the oxide ceramic crucible 2. As shown in FIG. 1, the oxide ceramic crucible 2 is installed in the accommodating section 1a.

[0040] As the oxide ceramic crucible 2, a known oxide ceramic crucible can be used. As a material of the oxide ceramic crucible 2, it is preferable to use a chemically stable oxide ceramic, and specifically, it is preferable to use calcia or yttria, and it is more preferable to use calcia, because the calcia or yttria is a material in which inclusions are less likely to be mixed. By using the oxide ceramic crucible 2 made of calcia or yttria, the amount of oxygen mixed in the molten raw material 3a (molten metal) from the oxide ceramic crucible 2 can be suppressed. Accordingly, even in a case where the addition amount of the deoxidation material including Ca added to the raw material 3 or the molten raw material 3a is small, the oxygen content in the TiAl alloy casting material obtained after casting can be sufficiently reduced.

[Melting step] [Deoxidation material adding step]

[0041] The method for manufacturing the TiAl alloy casting material according to the present embodiment includes a melting step. In the melting step, the raw material 3 is melted to obtain the molten raw material 3a (molten metal). In the present embodiment, the raw material 3 is melted in the oxide ceramic crucible 2 installed in the atmospheric melting furnace 1 under an air atmosphere. As will be described below, the raw material 3 is melted by covering an opening portion of the oxide ceramic crucible 2 with a funnel-shaped mold 5 and then creating an argon atmosphere in the oxide ceramic crucible 2. As will be described below, argon can be supplied to the oxide ceramic crucible 2, for example, using a gas supply pipe 7, or the like, inserted into the oxide ceramic crucible 2, via the funnel-shaped mold 5.

[0042] In the melting step, as shown in FIG. 1, a portion of the raw material 3 is put into the oxide ceramic crucible 2. Moreover, the entire amount of the deoxidation material including Ca is added to the oxide ceramic crucible 2, and then the raw material 3 is melted.

(Raw material)

[0043] The raw material 3 contains Ti and Al. As the raw material 3, in addition to Ti and Al, one or two or more kinds of elements selected from, for example, Nb, Cr, Mo, V, Mn, W, Fe, Si, C, and B may be contained as an additive element. The composition of the raw material 3 can be appropriately determined according to the use of the TiAl alloy casting material obtained after casting.

[0044] As the raw material 3, for example, a material containing 31.9 mass% to 34.2 mass% of Al, 4.0 mass% to 5.4 mass% of Nb, 2.3 mass% to 3.0 mass% of Cr, and 0.1 mass% to 0.5 mass% of oxygen, with the balance being Ti and impurities, can be used.

[0045] The raw material 3 contains impurities at a concentration that does not impair the use of the manufactured TiAl alloy casting material that is the target product. For example, in the case where a TiAl alloy casting material to be a turbine blade for a jet engine and a turbine wheel are cast, it is preferable that the impurities contained in the raw material 3 are within a range of a content that satisfies the component specifications (material specifications of each product) of the TiAl alloy in the manufactured TiAl alloy casting material.

[0046] The composition of the raw material 3 does not match the composition of the TiAl alloy casting material obtained after casting. Specifically, this is because, in a manufacturing step of the TiAl alloy casting material, there are elements that increase by being mixed in the molten raw material 3a from the oxide ceramic crucible 2 in contact with the molten raw material 3a, the atmosphere, or the like, elements that increase by being added with a deoxidation material including Ca, and elements that are discharged as a fume from the molten raw material 3a and decrease.

[0047] In the method for manufacturing the TiAl alloy casting material according to the present embodiment, Ti and Al, which are the main elements of the TiAl alloy, are hardly mixed from the device and the atmosphere or hardly discharged in a manufacturing process. Accordingly, the increase and decrease in the amount of Ti accompanying the manufacturing step of the TiAl alloy casting material is almost none. Therefore, the mass of Ti used as the raw material 3 and the mass of Ti contained in the TiAl alloy casting material obtained after casting can be regarded as the same. Meanwhile, the amount of Al is increased by using an AlCa alloy as the deoxidation material including Ca in the manufacturing step of the TiAl alloy casting material and is decreased by being discharged from the molten metal as a fume such as $CaAl_2O_4$ in the deoxidation step.

[0048] In addition, in the method for manufacturing the TiAl alloy casting material according to the present embodiment, for Nb and Cr that may be included in the raw material 3 as the additive elements, similar to Ti, it is rare that the Nb and Cr are mixed in from the device and the atmosphere or discharged in the manufacturing process. Accordingly, the increase and decrease in the amount of Nb and the amount of Cr accompanying the manufacturing step of the TiAl alloy casting material are almost none. Therefore, the masses of Nb and Cr used as the raw material 3 and the masses of Nb and Cr contained in the TiAl alloy casting material obtained after casting can be regarded as the same.

[0049] In a case where the composition of the raw material 3 contains, for example, 31.9 mass% to 34.2 mass% of Al, 4.0 mass% to 5.4 mass% of Nb, 2.3 mass% to 3.0 mass% of Cr, 0.1 mass% to 0.5 mass% of oxygen, and the balance of Ti and impurities, after casting, a TiAl alloy casting material containing 31.9 mass% to 34.2 mass% of Al, 4.0 mass% to 5.4 mass% of Nb, 2.3 mass% to 3.0 mass% of Cr, 0.04 mass% to 0.12 mass% of oxygen, and 0.01 mass% to 0.07 mass% of Ca, with the balance being Ti and impurities, is easily obtained, which is preferable. Since a TiAl alloy casting material having such a composition has excellent impact resistance characteristics, and has favorable machinability, tensile strength, and creep strength, the TiAl alloy casting material can be suitably used as a material for a turbine blade for a jet engine and a turbine wheel.

[0050] The content of Al contained in the raw material 3 can be, for example, 31.9 mass% to 34.2 mass%, and is preferably 32.9 mass% to 33.8 mass%. This is because the impact resistance, tensile strength, and creep strength of the TiAl alloy casting material obtained after casting are better.

[0051] The content of Nb contained in the raw material 3 can be, for example, 4.0 mass% to 5.4 mass%, and is preferably

4.4 mass% to 5.0 mass%. This is because the oxidation resistance of the TiAl alloy casting material obtained after casting is better.

[0052] In addition, the content of Cr contained in the raw material 3 can be, for example, 2.3 mass% to 3.0 mass%, and is preferably 2.5 mass% to 2.8 mass%. This is because the ductility of the TiAl alloy casting material obtained after casting is better.

[0053] In a case where the raw material 3 includes 4.4 mass% to 5.0 mass% of Nb and 2.5 mass% to 2.8 mass% of Cr in addition to Ti and Al, a TiAl alloy casting material having more excellent impact resistance characteristics and having more excellent machinability, tensile strength, and creep strength is obtained.

[0054] The shape of the raw material 3 is not particularly limited and, for example, a metal element raw material such as sponge titanium, Al granules (pellets), Nb foil, and Cr granules, and/or a mother alloy ingot (casting block) made using these metal element raw materials can be used.

[0055] The raw material 3 may contain a TiAl alloy scrap. Examples of the TiAl alloy scraps include TiAl alloy cutting chips and TiAl alloy casting scraps. Examples of the TiAl alloy cutting chips include cutting chips generated in a case where a member such as a turbine blade for a jet engine is manufactured from the TiAl alloy casting material. In addition, examples of the TiAl alloy casting scraps include casting scraps made of parts that do not become a product of the TiAl alloy casting material, such as a runner generated in the case where precision casting of a TiAl alloy using lost wax casting is performed.

[0056] In the case where the TiAl alloy cutting chips are used as the raw material 3, in order to further reduce the oxygen content included in the TiAl alloy casting material obtained after casting, it is preferable that the TiAl alloy cutting chips are used after an organic substance such as a coolant or a cutting oil adhering to the TiAl alloy cutting chips is washed by using an organic solvent such as acetone. As the method for washing the TiAl alloy cutting chips by using the organic solvent, for example, a known method such as a method using an ultrasonic cleaner can be used. In addition, in the case where the TiAl alloy casting scraps are used as the raw material 3, in order to further reduce the oxygen content included in the TiAl alloy casting material obtained after casting, it is preferable that the TiAl alloy casting scraps are used after the surface thereof is pickled.

(Deoxidation material including Ca)

[0057] As the deoxidation material including Ca, for example, Ca in a monomeric state may be used, or a compound including Ca, such as an AlCa alloy, CaF_2, or $CaCl_2$, may be used. As the deoxidation material including Ca, the AlCa alloy is preferable because the AlCa alloy is solid and thus easy to handle, special consideration is not required for storage, and special consideration is not required for safety.

[0058] As the AlCa alloy, since the variation in the Ca content in the manufacturing process of the AlCa alloy is small and the AlCa alloy can be manufactured stably, an AlCa alloy having a Ca content of 3 mass% to 20 mass% is preferably used, an AlCa alloy having a Ca content of 10 mass% or 5 mass% is more preferably used, and an AlCa alloy having a Ca content of 5 mass% is still more preferably used.

[0059] The deoxidation material including Ca is added such that the Ca concentration in the total mass of the raw material 3 and the deoxidation material is 0.2 mass% to 1.0 mass%. The addition amount of the deoxidation material including Ca can be appropriately determined within the above range according to the composition of the raw material 3, the composition range of the TiAl alloy casting material that is the target product, conditions such as the atmosphere, temperature, and time for heating the molten raw material 3a including the deoxidation material, and the like. By adding the deoxidation material including Ca to the raw material 3 such that the Ca concentration in the total mass of the raw material 3 and the deoxidation material is within the above-described range, after casting, a TiAl alloy casting material containing 0.04 mass% to 0.12 mass% of oxygen and 0.01 mass% to 0.07 mass% of Ca and having excellent impact resistance characteristics is obtained. In the method for manufacturing the TiAl alloy casting material according to the present embodiment, since the Ca concentration in the total mass of the raw materials 3 and the deoxidation material is set to 0.2 mass% or more, the effect resulting from adding the deoxidation material is sufficiently obtained, and the oxygen content of the TiAl alloy casting material obtained after casting is 0.12 mass% or less. In addition, since the Ca concentration in the total mass of the raw material 3 and the deoxidation material is set to 1.0 mass% or less, the Ca content remaining in the TiAl alloy casting material obtained after casting is 0.07 mass% or less.

[0060] In addition, the deoxidation material including Ca may be added such that the Ca concentration in the total mass of the raw material 3 and the deoxidation material is 0.4 mass% to 0.8 mass%. By setting the addition amount of the deoxidation material including Ca to be within the above range and appropriately adjusting the composition of the raw material 3 and the conditions, such as the atmosphere, temperature, and time for heating the molten raw material 3a including the deoxidation material, a TiAl alloy casting material having an oxygen content of 0.04 mass% to 0.10 mass% and a Ca content of 0.01 mass% to 0.03 mass% after casting and having more excellent impact resistance characteristics is obtained.

[0061] The deoxidation material including Ca may be added such that the Ca concentration in the total mass of the raw material 3 and the deoxidation material is 0.55 mass% to 0.65 mass%.

[0062] Next, as shown in FIG. 2, the funnel-shaped mold 5 is installed on the furnace wall 1b of the atmospheric melting furnace 1 with the wider opening portion of the funnel-shaped mold 5 facing the oxide ceramic crucible 2 to cover the opening portion of the oxide ceramic crucible 2 (mold installation step). The wider opening portion of the funnel-shaped mold 5 functions as a pouring port for pouring the molten raw material 3a into the funnel-shaped mold 5 in a casting step described below. It is preferable to use a funnel-shaped mold 5 of which the internal volume is larger than the volume of the raw material 3.

[0063] As the funnel-shaped mold 5, a mold made of a known material used in a case where the TiAl alloy casting material is manufactured can be used. Specifically, as the funnel-shaped mold 5, it is possible to use a mold or the like made of cast iron, carbon steel, or the like, and having a double-split structure with an inner surface coated with a ceramic such as zircon to prevent a reaction with the molten raw material 3a.

[0064] In the present embodiment, the case where the mold is used as the funnel-shaped mold 5 has been described as an example. However, the lost wax casting may be performed using a ceramic mold made of alumina, silica, mullite, zirconia, or the like, as the funnel-shaped mold 5. By performing the lost wax casting, a TiAl alloy casting material having a shape close to the final product is obtained.

[0065] In addition, as shown in FIG. 2, it is preferable that a simple sealing material 6 made of cement or the like is installed at a contact portion between the funnel-shaped mold 5 and the furnace wall 1b of the atmospheric melting furnace 1. This makes it possible to suppress the entry of air into the oxide ceramic crucible 2 from the contact portion between the funnel-shaped mold 5 and the furnace wall 1b of the atmospheric melting furnace 1.

[0066] Next, the gas supply pipe 7 is inserted into a narrower opening portion of the funnel-shaped mold 5, and Ar gas is supplied into the oxide ceramic crucible 2 via the gas supply pipe 7 (atmosphere replacement step). The Ar gas is a gas heavier than air. For this reason, in a case where the Ar gas is supplied into the oxide ceramic crucible 2, the Ar gas is accumulated from the bottom of the oxide ceramic crucible 2, and the air is discharged through the funnel-shaped mold 5. Accordingly, the inside of the funnel-shaped mold 5 and the inside of the oxide ceramic crucible 2 are replaced with an Ar atmosphere, and the contact between the molten raw material 3a obtained by melting the raw material 3 and the air can be avoided.

[0067] Thereafter, the oxide ceramic crucible 2 is heated using the high-frequency coil 4 installed in the atmospheric melting furnace 1, and as shown in FIG. 3, the raw material 3 is melted to obtain the molten raw material 3a (heating step). In the present embodiment, it is preferable that the Ar gas is continuously supplied into the oxide ceramic crucible 2 until immediately before the installation (see FIG. 5) of a lid 5a at the narrower opening portion of the funnel-shaped mold 5 even after the inside of the funnel-shaped mold 5 and the inside of the oxide ceramic crucible 2 are replaced with the Ar atmosphere. Accordingly, it is possible to effectively suppress the mixing of oxygen in the air into the molten raw material 3a, and it is possible to further reduce the oxygen content in the TiAl alloy casting material obtained after casting.

[0068] In the melting step of the present embodiment, it is preferable that the raw material 3 is melted while observing the inside of the oxide ceramic crucible 2 from the narrower opening portion of the funnel-shaped mold 5 by visual observation or using a camera. Accordingly, the melting situation of the raw material 3 and whether or not all of the raw material 3 is melted can be confirmed.

[0069] Next, in the melting step of the present embodiment, as shown in FIG. 4, the funnel 8 is installed at the narrower opening portion of the funnel-shaped mold 5, and the remaining raw material 3 is added to the oxide ceramic crucible 2 once or multiple times via the funnel 8 and the narrower opening portion of the funnel-shaped mold 5.

[0070] In the method for manufacturing the TiAl alloy casting material according to the present embodiment, the case where a portion of the raw material 3 is put into the oxide ceramic crucible 2 to be melted as a molten metal, and the remaining raw material 3 is added to the oxide ceramic crucible 2 once or multiple times has been described as an example. However, after all of the raw material 3 is put into the oxide ceramic crucible 2, the raw material 3 may be melted, or while a portion of the raw material 3 is put into the oxide ceramic crucible 2 to be melted, the remaining raw material 3 may be added to the oxide ceramic crucible 2 once or multiple times.

[0071] In the case where the raw material 3 is added to the oxide ceramic crucible 2 multiple times, different raw materials 3 may be added each time, the same raw materials 3 may be added some of the multiple times, or the same raw materials 3 may be added each time. This can be appropriately determined according to the composition, shape, and the like of the raw material 3.

[0072] In addition, in the method for manufacturing the TiAl alloy casting material according to the present embodiment, the entire amount of the deoxidation material including Ca is added to the oxide ceramic crucible 2 together with the raw material 3. However, the deoxidation material including Ca may be added to the molten raw material 3a (molten metal) in the oxide ceramic crucible 2 via the funnel-shaped mold 5.

[0073] In addition, in the method for manufacturing the TiAl alloy casting material according to the present embodiment, the deoxidation material including Ca may be added to the raw material 3 and/or the molten raw material 3a multiple times. That is, a portion of the deoxidation material including Ca may be put into the oxide ceramic crucible 2 together with the raw material 3, and the remaining deoxidation material including Ca may be added to the molten raw material 3a put into the oxide ceramic crucible 2 via the funnel-shaped mold 5 once or multiple times.

[Deoxidation step]

[0074] In the present embodiment, after confirming that all of the raw material 3 is melted, in the deoxidation step, the molten raw material 3a including the deoxidation material is heated and melted in the oxide ceramic crucible 2 of which the opening portion is covered with the funnel-shaped mold 5, and the molten state is maintained. Accordingly, the components contained in the molten raw material 3a are homogenized. Along with this, a fume containing a reaction product of oxygen and Ca in the molten raw material 3a is generated and discharged via the funnel-shaped mold 5 to remove the oxygen in the molten raw material 3a.

[0075] The time for heating and holding the molten raw material 3a including the deoxidation material in a molten state is, for example, preferably 2 minutes to 10 minutes, and more preferably 3 minutes to 5 minutes, after all the raw material 3 is melted to be the molten raw material 3a including the deoxidation material. In the case where the time for holding the molten raw material 3a including the deoxidation material in a molten state is 2 minutes or longer, the reaction between the oxygen and Ca in the molten raw material 3a sufficiently proceeds. As a result, the generation of the fume containing the reaction product of oxygen and Ca in the molten raw material 3a is promoted, and the effect of removing the oxygen in the molten raw material 3a is more remarkable. In the case where the time for heating the molten raw material 3a including the deoxidation material and holding the molten raw material 3a in a molten state is 10 minutes or less, the oxygen content in the TiAl alloy casting material obtained after casting can be reduced without impairing the productivity of the TiAl alloy casting material.

[0076] The temperature at which the molten raw material 3a including the deoxidation material is heated and held in a molten state is preferably 1650°C to 1750°C, and more preferably 1675°C to 1725°C. In the case where the temperature at which the molten raw material 3a including the deoxidation material is held in a molten state is 1650°C or higher, the reaction between the oxygen and Ca in the molten raw material 3a is promoted, and the generation of the fume containing the reaction product is promoted. Therefore, the effect of removing the oxygen in the molten raw material 3a is more remarkable. In the case where the temperature at which the molten raw material 3a including the deoxidation material is heated and held in a molten state is 1750°C or lower, the reaction between the oxide ceramic crucible 2 and the molten raw material 3a is suppressed, which is preferable.

[0077] In the present embodiment, it is preferable that the deoxidation step is performed by heating the raw material 3 in the oxide ceramic crucible 2 by using the high-frequency coil 4, melting the raw material 3 put into the oxide ceramic crucible 2 to obtain the molten raw material 3a including the deoxidation material, and then continuing the heating of the molten raw material 3a to maintain the molten state of the molten raw material 3a. Accordingly, the TiAl alloy casting material can be efficiently manufactured.

[0078] In the present embodiment, after the deoxidation step, as shown in FIG. 5, the lid 5a is installed in the narrower opening portion of the funnel-shaped mold 5. As the lid 5a, for example, one made of cast iron, carbon steel, or the like, can be used, with the inner surface coated with a ceramic such as zircon to prevent a reaction with the molten raw material 3a.

[0079] Thereafter, in the present embodiment, as shown in FIG. 6, the atmospheric melting furnace 1 is turned upside down in a state in which the oxide ceramic crucible 2 and the funnel-shaped mold 5 are integrated with each other, and the molten raw material 3a is poured into the funnel-shaped mold 5 from the oxide ceramic crucible 2 and cooled (casting step). Accordingly, the TiAl alloy casting material 3b is obtained.

[0080] Thereafter, as shown in FIG. 7, the TiAl alloy casting material 3b is taken out from the funnel-shaped mold 5 and cut to be divided into a product part 3c made of a part to be a product, and a reuse part 3e that is formed with a riser 3d and made of a part not to be a product. The reuse part 3e is TiAl alloy casting scraps and can be reused as the raw material 3 of the TiAl alloy casting material 3b.

(Other examples)

[0081] The method for manufacturing the TiAl alloy casting material according to the present embodiment is not limited to the above-described embodiment.

[0082] For example, in the above-described embodiment, as an example of the method for manufacturing the TiAl alloy casting material, the case where the device including the oxide ceramic crucible 2 installed in the atmospheric melting furnace 1 shown in FIG. 1 is used has been described. However, a vacuum melting furnace may be used instead of the atmospheric melting furnace. As the vacuum melting furnace, a known vacuum melting furnace can be used and, for example, a general vacuum induction melting furnace (VIM furnace) can be used.

[0083] In the case where the vacuum melting furnace is used, it is preferable to use the following method. That is, in the deoxidation material adding step, the entire amount of the deoxidation material is put into the oxide ceramic crucible installed in the vacuum melting furnace together with the raw material. Then, the inside of the vacuum melting furnace is replaced with an Ar gas atmosphere by evacuating the inside of the vacuum melting furnace and then supplying Ar gas. Then, in the melting step, the entire amount of the raw material is melted in the oxide ceramic crucible installed in the vacuum melting furnace under the Ar atmosphere to obtain a molten metal.

[0084] In the case where the vacuum melting furnace is used, it is preferable to melt the raw material 3 while observing the inside of the oxide ceramic crucible 2 through a quartz window installed in the vacuum induction melting furnace by using a camera installed above the vacuum induction melting furnace. Accordingly, the melting situation of the raw material 3 and whether or not all of the raw material 3 is melted can be confirmed.

[0085] Thereafter, in the deoxidation step, oxygen in the molten metal is removed by heating the molten metal including the deoxidation material in the oxide ceramic crucible installed in the vacuum melting furnace under the Ar atmosphere for maintaining a molten state.

[0086] The method for manufacturing the TiAl alloy casting material according to the present embodiment includes the deoxidation material adding step of adding the deoxidation material including Ca to either or both of the raw material 3 containing Ti and Al and various additive elements and the molten raw material 3a obtained by melting the raw material 3, and of adding the deoxidation material such that the Ca concentration in the total mass of the raw material 3 and the deoxidation material is 0.2 mass% to 1.0 mass%; and the deoxidation step of heating the molten raw material 3a including the deoxidation material for maintaining a molten state to generate the fume containing the reaction product of oxygen and Ca in the molten raw material 3a to remove the oxygen in the molten raw material 3a. For this reason, the TiAl alloy casting material obtained by performing the above-described casting step after the deoxidation step contains 0.04 mass% to 0.12 mass% of oxygen and 0.01 mass% to 0.07 mass% of Ca and has excellent impact resistance characteristics.

[0087] Accordingly, according to the method for manufacturing the TiAl alloy casting material according to the present embodiment, the TiAl alloy casting material having a sufficiently low oxygen content can be obtained without using a special device or using a special raw material having a low oxygen content. Specifically, in the method for manufacturing the TiAl alloy casting material according to the present embodiment, various devices such as a device including the oxide ceramic crucible 2 installed in an atmospheric melting furnace 1 or a vacuum melting furnace, and various raw materials such as the TiAl alloy cutting chips, the TiAl alloy casting scraps, and the TiAl alloy scraps having a large amount of oxygen can be used without limitation.

[TiAl alloy casting material]

[0088] The TiAl alloy casting material according to the present embodiment contains 0.04 mass% to 0.10 mass% of oxygen and 0.01 mass% to 0.03 mass% of Ca. Since the TiAl alloy casting material according to the present embodiment has an oxygen content of 0.10 mass% or less and a Ca content of 0.03 mass% or less, the TiAl alloy casting material has excellent impact resistance characteristics. In addition, since the oxygen content is 0.04 mass% or more, in a case where manufacture is performed by using the method for manufacturing the TiAl alloy casting material according to the present embodiment, the amount of the deoxidation material including Ca used can be suppressed. As a result, the Ca content in the TiAl alloy casting material can be set to 0.03 mass% or less. In addition, since the Ca content is 0.01 mass% or more, in a case where manufacture is performed by using the method for manufacturing the TiAl alloy casting material according to the present embodiment, a sufficient amount of the usable deoxidation material including Ca can be secured, and the deoxidizing effect resulting from the addition of the deoxidation material can be sufficiently obtained. For this reason, various devices including the oxide ceramic crucible 2 installed in an atmospheric melting furnace 1 or a vacuum melting furnace, various raw materials such as the TiAl alloy cutting chips and the TiAl alloy casting scraps can be used.

[0089] The TiAl alloy casting material of the present embodiment may be one containing 31.9 mass% to 34.2 mass% of Al, 4.0 mass% to 5.4 mass% of Nb, 2.3 mass% to 3.0 mass% of Cr, 0.04 mass% to 0.12 mass% of oxygen and 0.01 mass% to 0.07 mass% of Ca, with the balance being Ti and impurities. Since such a TiAl alloy casting material has excellent impact resistance characteristics, and has favorable machinability, tensile strength, and creep strength, the TiAl alloy casting material can be suitably used for a material for a turbine blade for a jet engine and a turbine wheel.

[0090] The TiAl alloy casting material according to the present embodiment may be one containing 32.9 mass% to 33.8 mass% of Al, 4.4 mass% to 5.0 mass% of Nb, 2.5 mass% to 2.8 mass% of Cr, 0.04 mass% to 0.12 mass% oxygen, and 0.01 mass% to 0.07 mass% of Ca, with the balance being Ti and impurities. Since such a TiAl alloy casting material has more excellent impact resistance characteristics, and has more excellent machinability, tensile strength, and creep strength, the TiAl alloy casting material is particularly suitable as a material for a turbine blade for a jet engine and a turbine wheel.

[0091] All the TiAl alloy casting materials of the present embodiment can be manufactured by appropriately changing the composition of the raw material 3, the type and the amount of the deoxidation material including Ca, and the conditions such as the atmosphere, temperature, and time for heating the molten raw material 3a including the deoxidation material by using the method for manufacturing the TiAl alloy casting material of the present embodiment described above.

[Turbine blade for jet engine] [Turbine wheel]

[0092] The turbine blade for a jet engine and the turbine wheel according to the present embodiment are made of the Al alloy casting material according to the present embodiment. Accordingly, the turbine blade for a jet engine and the turbine wheel have excellent impact resistance characteristics.

[0093] The turbine blade for a jet engine and the turbine wheel according to the present embodiment can be manufactured by, for example, cutting the Al alloy casting material according to the present embodiment by using a known method. The TiAl alloy cutting chips generated in a case where the TiAl alloy casting material is cut are casting scraps and can be reused as the raw material 3 of the TiAl alloy casting material 3b.
[0094] Although the embodiment of the present invention has been described above in detail, the components, combinations thereof, and the like, in each embodiment are examples, and additions, omissions, replacements, and other changes of the components may be made within a range without departing from the spirit of the present invention.

EXAMPLES

[Experimental Example 1]

[0095] The atmospheric melting furnace 1 of a roll-over furnace type shown in FIG. 1 was used, and the oxide ceramic crucible 2 made of calcia was installed in the atmospheric melting furnace 1.
[0096] Each of metal element raw materials made of sponge titanium (trade name: TST-1; manufactured by Toho Titanium Co., Ltd.), Al granules (pellets) (manufactured by Furuuchi Chemical Corporation), Nb foil (manufactured by Raremetal Co., Ltd.), and Cr granules (manufactured by Furuuchi Chemical Corporation) was prepared. In addition, as the deoxidation material including Ca, an AlCa alloy having a Ca content of 5 mass% was prepared.
[0097] A deoxidation-material-containing raw material of Experimental Example 1 consisting of 0.10 mass% of Ca was prepared by weighing each of the above metal element raw materials, preparing a raw material containing 33.4 mass% of Al, 4.8 mass% of Nb, and 2.7 mass% of Cr, and the balance of Ti and impurities, and adding the deoxidation material including Ca to the raw material.
[0098] That is, the Al content in the deoxidation-material-containing raw material of Experimental Example 1 is the ratio of the total amount of the Al granules contained in the deoxidation-material-containing raw material and the amount of Al in the AlCa alloy.
[0099] Then, 500 g of the deoxidation-material-containing raw material of Experimental Example 1 was put into the oxide ceramic crucible 2.
[0100] Next, as shown in FIG. 2, the funnel-shaped mold 5 was installed on the furnace wall 1b of the atmospheric melting furnace 1 with the wider opening portion of the funnel-shaped mold 5 facing the oxide ceramic crucible 2 to cover the opening portion of the oxide ceramic crucible 2 (mold installation step). As the funnel-shaped mold 5, a mold made of carbon steel and having a double-split structure with an inner surface coated with zirconium paint (trade name; Oka Paint 308; manufactured by Okazaki Mineral Products Co., Ltd.) was used.
[0101] Next, as shown in FIG. 2, the sealing material 6 made of cement was installed at the contact portion between the funnel-shaped mold 5 and the furnace wall 1b of the atmospheric melting furnace 1.
[0102] Next, the gas supply pipe 7 was inserted into the narrower opening portion of the funnel-shaped mold 5, and Ar gas was supplied into the oxide ceramic crucible 2 via the gas supply pipe 7 (atmosphere replacement step). The supply of the Ar gas into the oxide ceramic crucible 2 was continuously performed until immediately before the installation of the lid 5a at the narrower opening portion of the funnel-shaped mold 5 (see FIG. 5).
[0103] Thereafter, the oxide ceramic crucible 2 was heated using the high-frequency coil 4 installed in the atmospheric melting furnace 1, and as shown in FIG. 3, the deoxidation-material-containing raw material was melted to prepare the molten raw material 3a (heating step).
[0104] The inside of the oxide ceramic crucible 2 was observed from the narrower opening portion of the funnel-shaped mold 5 by using a camera to confirm that all of the deoxidation-material-containing raw material was melted. Even after that, the oxide ceramic crucible 2 was continuously heated, and a molten state of the molten raw material 3a including the deoxidation material after all the deoxidation-material-containing raw material was melted was maintained at 1700°C for 3 minutes (deoxidation step).
[0105] Thereafter, as shown in FIG. 5, the lid 5a was installed in the narrower opening portion of the funnel-shaped mold 5. As the lid 5a, a carbon steel lid having an inner surface coated with zirconium paint (trade name; Oka Paint 308; manufactured by Okazaki Mineral Products Co., Ltd.) was used.
[0106] Thereafter, as shown in FIG. 6, the atmospheric melting furnace 1 was turned upside down in a state in which the atmospheric-melting furnace 1 and the funnel-shaped mold 5 were integrated with each other, and the molten raw material 3a was poured into the funnel-shaped mold 5 from the oxide ceramic crucible 2 and cooled (casting step). Accordingly, a TiAl alloy casting material 3b of Experimental Example 1, which was a substantially columnar ingot having a diameter of 40 mm and a length of 100 mm, was obtained.

[Experimental Example 2 to Experimental Example 5]

[0107] Deoxidation-material-containing raw materials including Ca in contents (addition amounts) shown in Table 1 were obtained by weighing the same raw material as that in Experimental Example 1 and adding the same deoxidation material including Ca as that in Experimental Example 1 to the raw material. Except for this, TiAl alloy casting materials 3b of Experimental Examples 2 to 5, which were substantially columnar ingots having a diameter of 40 mm and a length of 100 mm, were obtained in the same manner as in Experimental Example 1.

[Experimental Example 6]

[0108] A TiAl alloy casting material 3b of Experimental Example 6, which was a substantially columnar ingot having a diameter of 40 mm and a length of 100 mm, was obtained in the same manner as in Experimental Example 1, except that the raw material of Experimental Example 1 was used instead of the deoxidation-material-containing raw material in Experimental Example 1.

[Experimental Example 7]

[0109] TiAl alloy cutting chips and TiAl alloy casting scraps having the same contents of Ti, Al, Nb, and Cr as the raw material in Experimental Example 1 were prepared. The TiAl alloy cutting chips were used after being subjected to ultrasonic cleaning using acetone. As the TiAl alloy casting scraps, scraps having pickled surfaces were used.

[0110] Then, the raw material of Experimental Example 7 was prepared with 25 mass% of the above-described metal element raw materials used as the raw material of Experimental Example 1 being the TiAl alloy cutting chips and 25 mass% thereof being the TiAl alloy casting scraps. A TiAl alloy casting material 3b of Experimental Example 7, which was a substantially columnar ingot having a diameter of 40 mm and a length of 100 mm, was obtained in the same manner as in Experimental Example 1, except that a deoxidation-material-containing raw material of Experimental Example 7 containing 0.10 mass% of Ca was prepared by adding a deoxidation material including Ca, which was the same as that in Experimental Example 1, to the raw material of Experimental Example 7.

[Experimental Example 8 to Experimental Example 11]

[0111] Deoxidation-material-containing raw materials including Ca in contents (addition amounts) shown in Table 1 were obtained by weighing the same raw material as that in Experimental Example 7 and adding the same deoxidation material including Ca as that in Experimental Example 1 to the raw material. Except for this, TiAl alloy casting materials 3b of Experimental Examples 8 to 11, which were substantially columnar ingots having a diameter of 40 mm and a length of 100 mm, were obtained in the same manner as in Experimental Example 7.

[Experimental Example 12]

[0112] A TiAl alloy casting material 3b of Experimental Example 12, which was a substantially columnar ingot having a diameter of 40 mm and a length of 100 mm, was obtained in the same manner as in Experimental Example 7, except that the raw material of Experimental Example 7 was used instead of the deoxidation-material-containing raw material in Experimental Example 7.

[Experimental Example 13]

[0113] Instead of the atmospheric melting furnace 1 shown in FIG. 1, a vacuum induction melting furnace (VIM furnace) was used, and the oxide ceramic crucible 2 made of calcia, which was the same as that in Experimental Example 1, was installed in the vacuum induction melting furnace. Then, in the same manner as in Experimental Example 1, 500 g of the deoxidation-material-containing raw material of Experimental Example 1 was put into the oxide ceramic crucible 2.

[0114] Next, the inside of the vacuum melting furnace was replaced with an Ar atmosphere by evacuating the inside of the vacuum melting furnace and then supplying Ar gas.

[0115] Thereafter, a molten raw material 3a was prepared by heating and melting the deoxidation-material-containing raw material in the oxide ceramic crucible 2 by using an induction heating device installed in the vacuum induction melting furnace (heating step). Then, the inside of the oxide ceramic crucible 2 installed in the vacuum induction melting furnace was observed through the quartz window installed in the vacuum induction melting furnace by using a camera installed on an upper part of the vacuum induction melting furnace, to confirm that all of the deoxidation-material-containing raw material was melted. Even after that, the oxide ceramic crucible 2 was continuously heated, and a molten state of the molten raw material 3a including the deoxidation material after all the deoxidation-material-containing raw material was melted was maintained at 1700°C for 3 minutes (deoxidation step).

[0116] Thereafter, the molten raw material 3a was poured into a mold, having a columnar inner surface, installed in the vacuum melting furnace from the oxide ceramic crucible 2 and cooled (casting step). Accordingly, a TiAl alloy casting material 3b of Experimental Example 13, which was a substantially columnar ingot having a diameter of 40 mm and a length of 100 mm, was obtained.

[Experimental Example 14 to Experimental Example 17]

[0117] Deoxidation-material-containing raw materials including Ca in contents (addition amounts) shown in Table 2 were obtained by weighing the same raw material as that in Experimental Example 1 and adding the same deoxidation material including Ca as that in Experimental Example 1 to the raw material. Except for this, TiAl alloy casting materials 3b of Experimental Examples 14 to 17, which were substantially columnar ingots having a diameter of 40 mm and a length of 100 mm, were obtained in the same manner as in Experimental Example 13.

[Experimental Example 18]

[0118] A TiAl alloy casting material 3b of Experimental Example 18, which was a substantially columnar ingot having a diameter of 40 mm and a length of 100 mm, was obtained in the same manner as in Experimental Example 13, except that the raw material of Experimental Example 1 were used instead of the deoxidation-material-containing raw material in Experimental Example 1.

[Experimental Example 19]

[0119] A TiAl alloy casting material 3b of Experimental Example 19, which was a substantially columnar ingot having a diameter of 40 mm and a length of 100 mm, was obtained in the same manner as in Experimental Example 13, except that the deoxidation-material-containing raw material of Experimental Example 7 was used.

[Experimental Example 20 to Experimental Example 23]

[0120] Deoxidation-material-containing raw materials including Ca in contents (addition amounts) shown in Table 2 were obtained by weighing the same raw material as that in Experimental Example 7 and adding the same deoxidation material including Ca as that in Experimental Example 1 to the raw material. Except for this, TiAl alloy casting materials 3b of Experimental Examples 20 to 23, which were substantially columnar ingots having a diameter of 40 mm and a length of 100 mm, were obtained in the same manner as in Experimental Example 13.

[Experimental Example 24]

[0121] A TiAl alloy casting material 3b of Experimental Example 24, which was a substantially columnar ingot having a diameter of 40 mm and a length of 100 mm, was obtained in the same manner as in Experimental Example 13, except that the raw material of Experimental Example 7 was used instead of the deoxidation-material-containing raw material in Experimental Example 7.

[0122] Tables 1 and 2 show the type of melting furnace used during manufacture, the material of the crucible, the atmosphere in the crucible during the heating of the crucible, Ca addition amount (Ca concentration in the deoxidation-material-containing raw material), TiAl alloy cutting chip addition amount (content in the deoxidation-material-containing raw material excluding the deoxidation material), and TiAl alloy casting scrap addition amount (content in the deoxidation-material-containing raw material excluding the deoxidation material), regarding each of the TiAl alloy casting materials of Experimental Examples 1 to 24.

[0123] In addition, Tables 1 and 2 describe the classification invention examples and comparative examples regarding the TiAl alloy casting materials of Experimental Examples 1 to 24.

[Measurement of oxygen content and Ca content]

[0124] The TiAl alloy casting materials 3b of Experimental Examples 1 to 24 obtained in this manner were analyzed using an infrared absorption device (trade name: EMGA-930; manufactured by HORIBA, Ltd.), and the oxygen contents were determined. In addition, the TiAl alloy casting materials 3b of Experimental Examples 1 to 24 were analyzed using a high-frequency inductively coupled plasma (ICP) emission spectrometric analyzer (trade name: ICP-OES: manufactured by HORIBA, Ltd.), and the Ca contents were obtained. The results thereof are listed in Tables 1 and 2.

[Charpy impact test]

[0125] The TiAl alloy casting material 3b of each of Experimental Examples 1 to 24 was subjected to the heat treatment of heating at 1200°C for 4 hours. The heat treatment conditions are conditions usually performed in a hot isostatic press (HIP) performed in a case where a turbine blade for a jet engine made of a TiAl alloy is manufactured. Thereafter, a test piece having a length of 55 mm and a square cross-sectional shape having a length of 10 mm length and a width of 10 mm was taken from a central portion of each TiAl alloy casting material 3b, and a Charpy impact test was performed at room temperature. The results thereof are listed in Tables 1 and 2.

[0126] In the Charpy impact test, a small tester having a capacity of 7.5 J (trade name: Impact Tester; manufactured by Toyo Seiki Seisakusho-sho, Ltd.) was used such that the measurement error was reduced. In addition, in the case where a notch is formed in the test piece, the impact values of all the experimental examples are very small values, and it is difficult to clearly evaluate the differences between the experimental examples. For this reason, the notch was not formed in the test piece.

(Evaluation standard value)

[0127] In the Charpy impact value of the TiAl alloy casting material 3b of each of Experimental Examples 1 to 24, those having a Charpy impact value of 2.0 J/cm^2 or more (evaluation standard value) are regarded as good products.

[0128] The evaluation standard value of the Charpy impact value of the TiAl alloy casting material was determined based on the test results shown below.

[0129] A TiAl alloy casting material to be a turbine blade for a jet engine in the related art was manufactured by the following method.

[0130] That is, a raw material consisting of 33.4 mass% of Al, 4.8 mass% of Nb, 2.7 mass% of Cr, 0.08 mass% of oxygen, and the balance of Ti and impurities was melted by a method using the raw material using a water-cooled copper crucible installed in a vacuum melting furnace under a vacuum atmosphere, and the molten raw material was poured into the same mold as that in Experimental Example 13, which was installed in the vacuum melting furnace, and cooled. Accordingly, three TiAl alloy casting materials for evaluation, which were substantially columnar ingots having a diameter of 40 mm and a length of 100 mm, were manufactured.

[0131] The Charpy impact test was conducted on each of the obtained three TiAl alloy casting materials for evaluation in the same manner as in Experimental Example 1. As a result, the Charpy impact value was in a range of 2.0 J/cm^2 to 2.5 J/cm^2.

[0132] From this, in a case where the Charpy impact value of the TiAl alloy casting material is 2.0 J/cm^2 or more, it can be evaluated that the TiAl alloy casting material has the same impact resistance characteristics as those of the TiAl alloy casting material that is the turbine blade for a jet engine in the related art. Therefore, the evaluation standard value of the Charpy impact value of the TiAl alloy casting material in each of the present experimental examples was set to 2.0 J/cm^2 or more.

[Table 1]

Experimental example	Classification	Melting conditions						Characteristic evaluation results of TiAl alloy casting material		
		Melting furnace	Atmosphere	Crucible	TiAl alloy cutting chip addition amount (mass%)	TiAl alloy casting scrap addition amount (mass%)	Ca addition amount (mass%)	Content (mass%) Oxygen	Content (mass%) Ca	Charpy impact value at test piece without notch cut out from material after 1200°C x 4h heat treatment (J/cm^2)
1	Comparative Example	Vacuum melting furnace	Ar reflux	Calcia	0.0	0.0	0.10	0.143	0.007	1.8
2	Invention Example	Vacuum melting furnace	Ar reflux	Calcia	0.0	0.0	0.30	0.117	0.014	2.5
3	Invention Example	Vacuum melting furnace	Ar reflux	Calcia	0.0	0.0	0.60	0.099	0.042	2.4
4	Invention Example	Vacuum melting furnace	Ar reflux	Calcia	0.0	0.0	0.90	0.074	0.060	2.8
5	Comparative Example	Vacuum melting furnace	Ar reflux	Calcia	0.0	0.0	1.10	0.052	0.078	1.5
6	Comparative Example	Vacuum melting furnace	Ar reflux	Calcia	0.0	0.0	-	0.197	0.000	1.3
7	Comparative Example	Vacuum melting furnace	Ar reflux	Calcia	25.0	25.0	0.10	0.144	0.007	1.6
8	Invention Example	Vacuum melting furnace	Ar reflux	Calcia	25.0	25.0	0.30	0.118	0.013	2.5
9	Invention Example	Vacuum melting furnace	Ar reflux	Calcia	25.0	25.0	0.60	0.100	0.039	2.7
10	Invention Example	Vacuum melting furnace	Ar reflux	Calcia	25.0	25.0	0.90	0.074	0.056	2.4
11	Comparative Example	Vacuum melting furnace	Ar reflux	Calcia	25.0	25.0	1.10	0.052	0.073	1.7
12	Comparative Example	Vacuum melting furnace	Ar reflux	Calcia	25.0	25.0	-	0.284	0.000	0.9

[Table 2]

Experimental example	Classification	Melting conditions						Characteristic evaluation results of TiAl alloy casting material		
								Content (mass%)		Charpy impact value at test piece without notch cut out from material after 1200°C x 4h heat treatment (J/cm²)
		Melting furnace	Atmosphere	Crucible	TiAl alloy cutting chip addition amount (mass%)	TiAl alloy casting scrap addition amount (mass%)	Ca addition amount (mass%)	Oxygen	Ca	
13	Comparative Example	Vacuum melting furnace	Ar	Calcia	0.0	0.0	0.10	0.124	0.008	1.7
14	Invention example	Vacuum melting furnace	Ar	Calcia	0.0	0.0	0.30	0.102	0.015	2.3
15	Invention example	Vacuum melting furnace	Ar	Calcia	0.0	0.0	0.60	0.086	0.045	2.6
16	Invention example	Vacuum melting furnace	Ar	Calcia	0.0	0.0	0.90	0.064	0.064	2.5
17	Comparative Example	Vacuum melting furnace	Ar	Calcia	0.0	0.0	1.10	0.045	0.084	1.6
18	Comparative Example	Vacuum melting furnace	Ar	Calcia	0.0	0.0	-	0.175	0.000	1.1
19	Comparative Example	Vacuum melting furnace	Ar	Calcia	25.0	25.0	0.10	0.136	0.007	1.6
20	Invention example	Vacuum melting furnace	Ar	Calcia	25.0	25.0	0.30	0.112	0.014	2.4
21	Invention example	Vacuum melting furnace	Ar	Calcia	25.0	25.0	0.60	0.095	0.041	2.8
22	Invention example	Vacuum melting furnace	Ar	Calcia	25.0	25.0	0.90	0.070	0.058	2.3
23	Comparative Example	Vacuum melting furnace	Ar	Calcia	25.0	25.0	1.10	0.050	0.076	1.7
24	Comparative Example	Vacuum melting furnace	Ar	Calcia	25.0	25.0	-	0.237	0.000	1.0

[0133] As shown in Tables 1 and 2, in all the TiAl alloy casting materials of the invention examples, in which the deoxidation material was added such that the Ca concentration in the total mass of the raw material and the deoxidation material was 0.2 mass% to 1.0 mass%, the oxygen content was 0.12 mass% or less, which was a specified (in-house specification) value, and the Ca content was in a range of 0.01 mass% to 0.07 mass%. In addition, in all the TiAl alloy casting materials of the invention examples, the Charpy impact value was 2.0 J/cm^2 or more, which was the evaluation standard value, and it was confirmed that the TiAl alloy casting materials of the invention examples had the same or higher impact resistance characteristics as the TiAl alloy casting material for a turbine blade for a jet engine in the related art.

[0134] From this, it was confirmed that, by using the manufacturing methods that are different from each other only in that the oxygen contents of the TiAl alloy casting materials (Experimental Examples 6, 12, 18, and 24) manufactured without adding the deoxidation material are within a range of 0.175 mass% to 0.284 mass%, and the deoxidation material is added such that the Ca concentration in the total mass of each raw material and the deoxidation material is 0.2 mass% to 1.0 mass%, the TiAl alloy casting materials containing 0.04 mass% to 0.10 mass% of oxygen and 0.01 mass% to 0.03 mass% of Ca are obtained.

[0135] In addition, from the results of Experimental Examples 1 to 24, it was confirmed that various devices and raw materials, such as a method for manufacturing the TiAl alloy casting material with the crucible kept in an Ar reflux atmosphere while the crucible is heated by using a device including the oxide ceramic crucible 2 installed in the atmospheric melting furnace 1 by adding the deoxidation material such that the Ca concentration in the total mass of the raw material and the deoxidation material was 0.2 mass% to 1.0 mass%, a method for manufacturing the TiAl alloy casting material with the crucible kept in an Ar atmosphere while the crucible is heated by using a device including the oxide ceramic crucible 2 installed in the vacuum melting furnace, and a method using the raw material containing the TiAl alloy cutting chips and the TiAl alloy casting scraps, could be used.

[0136] More specifically, in Experimental Example 1 and Experimental Example 13, since the Ca concentration in the total mass of the raw material and the deoxidation material was 0.1 weight%, the deoxidizing effect of Ca was insufficient, and the oxygen content exceeded the specified value. As a result, the Charpy impact value was a value of less than 2.0 J/cm^2, which was the evaluation standard value.

[0137] In Experimental Example 5 and Experimental Example 17, since the Ca concentration in the total mass of the raw material and the deoxidation material is 1.1 weight%, the oxygen concentration is low, but the content of Ca is high. As a result, the Charpy impact value was a value of less than 2.0 J/cm^2, which was the evaluation standard value.

[0138] In addition, in Experimental Example 7 and Experimental Example 19 in which the raw materials containing the TiAl alloy cutting chips and the TiAl alloy casting scraps were used, similar to Experimental Example 1 and Experimental Example 13, the Ca concentration in the total mass of the raw material and the deoxidation material was 0.1 weight%. Therefore, the deoxidizing effect of Ca was insufficient, and the oxygen content was higher than the specified value. As a result, the Charpy impact value was a value of less than 2.0 J/cm^2, which was the evaluation standard value.

[0139] In addition, in Experimental Example 11 and Experimental Example 23 in which the raw material containing the TiAl alloy cutting chips and the TiAl alloy casting scraps was used, similar to Experimental Example 5 and Experimental Example 17, the Ca concentration in the total mass of the raw material and the deoxidation material was 1.1 weight%. Therefore, the oxygen concentration was low, but the content of Ca was high. As a result, the Charpy impact value was a value of less than 2.0 J/cm^2, which was the evaluation standard value.

[Industrial Applicability]

[0140] A TiAl alloy casting material having a sufficiently low oxygen content can be obtained without using a special device, a special material, or the like.

[Reference Signs List]

[0141]

1: Atmospheric melting furnace
1a: Accommodating section
1b: Furnace wall
2: Oxide ceramic crucible
3: Raw material
3a: Molten raw material
3b: TiAl alloy casting material
3c: Product part
3d: Riser
3e: Reuse part
4: High-frequency coil
5: Funnel-shaped mold
5a: Lid
6: Sealing material
7: Gas supply pipe
8: Funnel

Claims

1. A method for manufacturing a TiAl alloy casting material, the method comprising:

   a melting step of melting a raw material including Ti and Al to prepare a molten metal;
   a deoxidation material adding step of adding a deoxidation material including Ca to either or both of the raw material and the molten metal, the deoxidation material being added such that the Ca concentration in the total mass of the raw material and the deoxidation material is 0.2 mass% to 1.0 mass%; and
   a deoxidation step of heating the molten metal including the deoxidation material for maintaining a molten state to generate a fume including a reaction product of oxygen and Ca in the molten metal, so that the oxygen in the molten metal is removed.

2. The method for manufacturing a TiAl alloy casting material according to Claim 1, wherein the deoxidation material is an AlCa alloy.

3. The method for manufacturing a TiAl alloy casting material according to Claim 1 or Claim 2,

   wherein the melting step is a step of melting the raw material in an oxide ceramic crucible,
   the deoxidation material adding step is either or both of a step of putting the deoxidation material into the oxide ceramic crucible together with the raw material, and a step of adding the deoxidation material to the molten metal put into the oxide ceramic crucible, and
   in the deoxidation step, the molten metal including the deoxidation material put into the oxide ceramic crucible is heated and melted.

4. The method for manufacturing a TiAl alloy casting material according to Claim 1 or Claim 2,

   wherein the deoxidation material adding step is a step of putting the deoxidation material into an oxide ceramic crucible installed in a vacuum melting furnace together with the raw material,
   the melting step is a step of melting the raw material in the oxide ceramic crucible installed in the vacuum melting furnace under an Ar atmosphere after the deoxidation material adding step, and
   in the deoxidation step, the molten metal including the deoxidation material is heated and melted in the oxide ceramic crucible installed in the vacuum melting furnace under the Ar atmosphere.

5. The method for manufacturing a TiAl alloy casting material according to Claim 3,

   wherein the oxide ceramic crucible is installed in an atmospheric melting furnace under an air atmosphere,
   the melting step includes a mold installation step of installing the wider opening portion of a funnel-shaped mold toward the oxide ceramic crucible to cover the opening portion of the oxide ceramic crucible; an atmosphere replacement step of supplying an Ar gas into the oxide ceramic crucible; and a heating step of heating the oxide ceramic crucible,
   the deoxidation material adding step is either or both of a step of putting the deoxidation material into the oxide ceramic crucible together with the raw material, and a step of adding the deoxidation material to the molten metal put into the oxide ceramic crucible via the funnel-shaped mold,
   in the deoxidation step, the molten metal including the deoxidation material is heated and melted in the oxide ceramic crucible of which the opening portion is covered with the funnel-shaped mold, the fume in the oxide ceramic crucible is discharged via the funnel-shaped mold, and
   after the deoxidation step, a casting step of turning the atmospheric melting furnace upside down in a state in which the oxide ceramic crucible and the funnel-shaped mold are integrated with each other, to pour the molten metal into the funnel-shaped mold from the oxide ceramic crucible and cool the molten metal is performed.

6. The method for manufacturing a TiAl alloy casting material according to any one of Claims 1 to 5, wherein the raw material includes either or both of TiAl alloy cutting chips and TiAl alloy casting scraps.

7. A TiAl alloy casting material comprising:
   0.04 mass% to 0.10 mass% of oxygen and 0.01 mass% to 0.03 mass% of Ca.

8. ATiAl alloy casting material comprising:
   31.9 mass% to 34.2 mass% of Al, 4.0 mass% to 5.4 mass% of Nb, 2.3 mass% to 3.0 mass% of Cr, 0.04 mass% to 0.12

mass% of oxygen, and 0.01 mass% to 0.07 mass% of Ca, with the balance being Ti and impurities.

9. A turbine blade for a jet engine made of the TiAl alloy casting material according to Claim 7 or Claim 8.

10. A turbine wheel made of the TiAl alloy casting material according to Claim 7 or Claim 8.

FIG. 1

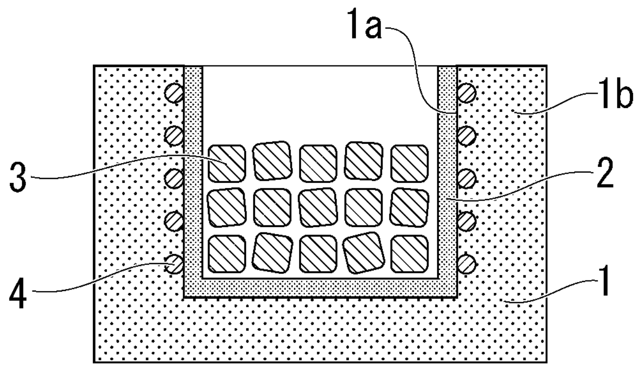


FIG. 2

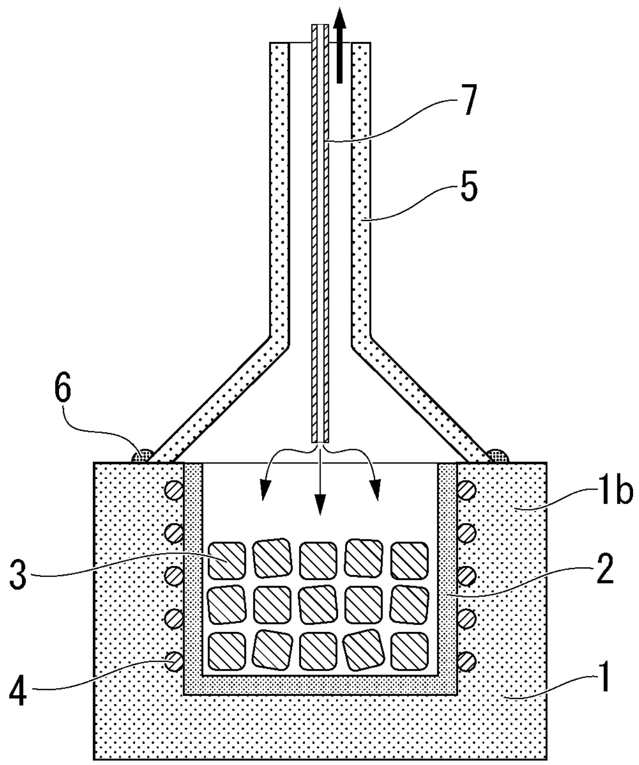


FIG. 3

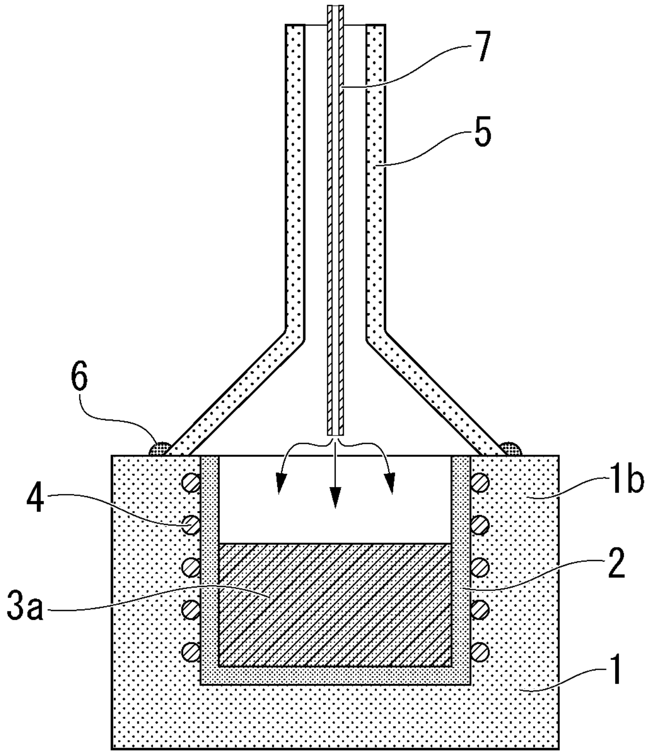


FIG. 4

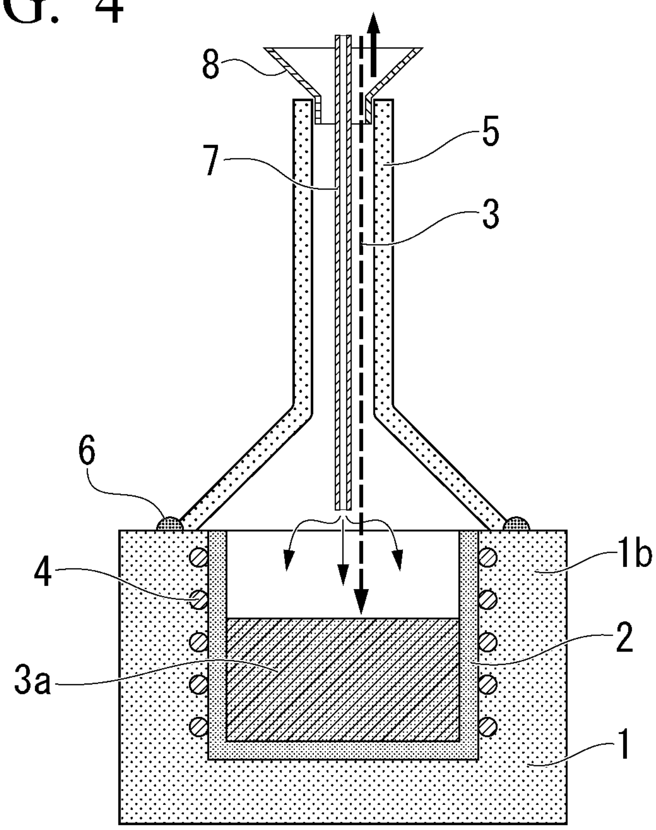


FIG. 5

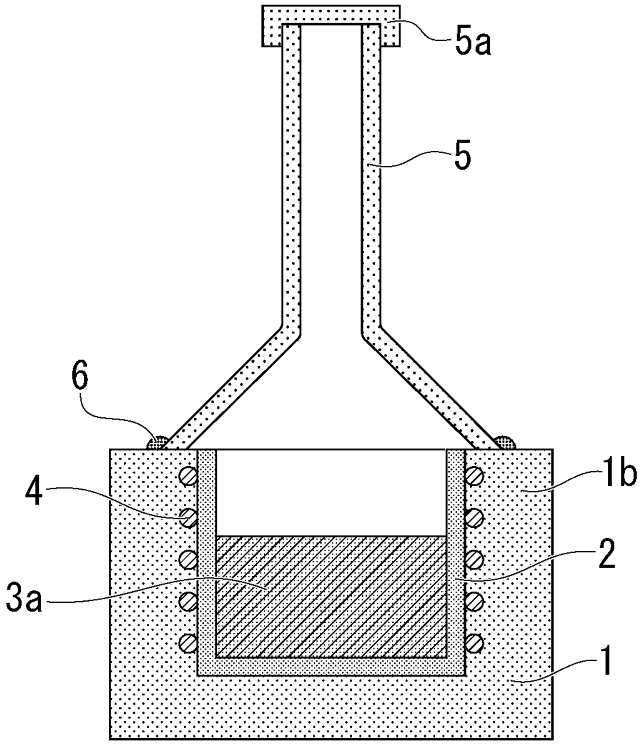


FIG. 6

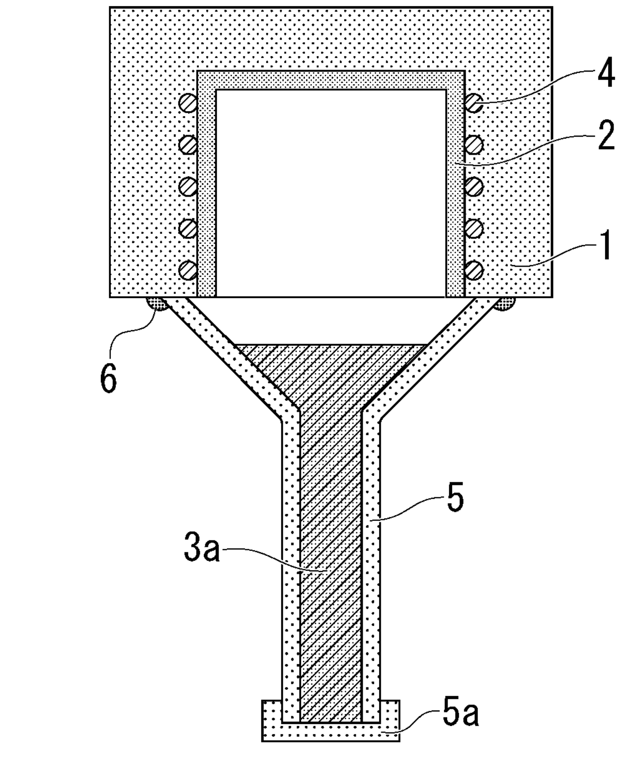
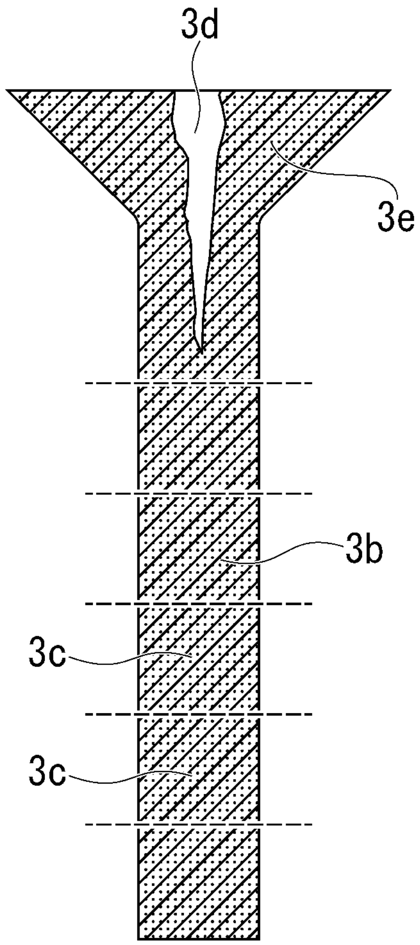


FIG. 7



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2023/011444

A. CLASSIFICATION OF SUBJECT MATTER

C22C 1/02(2006.01)i; ***B22D 21/04***(2006.01)i; ***B22D 23/00***(2006.01)i; ***C22B 7/00***(2006.01)i; ***C22B 9/10***(2006.01)i; ***C22C 14/00***(2006.01)i
FI: C22C1/02 503E; B22D21/04 Z; B22D23/00 C; C22B7/00 F; C22B9/10 101; C22C14/00 Z

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)

C22C1/02; B22D21/04; B22D23/00; C22B7/00; C22B9/10; C22C14/00

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 1971-2023
Registered utility model specifications of Japan 1996-2023
Published registered utility model applications of Japan 1994-2023

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 05-140669 A (KOBE STEEL LTD) 08 June 1993 (1993-06-08) claims 1-3, paragraphs [0010]-[0022], table 1	1, 3-4
Y		2, 6
A		5, 7-10
Y	芝田智樹ら, ＴｉＡｌの脱酸, 電気製鋼, 05 February 1993, vol. 64, no. 1, pp. 32-39 pp. 32-33, left column, p. 35, left column to p. 38, fig. 5, (SHIBATA, Tomoki et al. Deoxidation of Titanium Aluminides. DENKI-SEIKO.)	2, 6, 8-10
A		1, 3-5, 7
X	SAKAMOTO, K. et. al. Change in Oxygen Contents of Titanium Aluminides by Vacuum Induction, Cold Crucible Induction and Electoron Beam Melting. ISIJ International. 15 May 1992, vol. 32, no. 5, pp. 616-624 p. 616, left column, p. 621, left column, fig. 14	7, 9-10
A		1-6, 8

☑ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
18 April 2023	**09 May 2023**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2023/011444

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2021/157628 A1 (KOBE STEEL LTD) 12 August 2021 (2021-08-12) paragraphs [0041]-[0048], fig. 1	8-10
A		1-7

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2023/011444

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 05-140669 A	08 June 1993	(Family: none)	
WO 2021/157628 A1	12 August 2021	JP 2021-122830 A	

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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- JP 2009113060 A **[0015]**
- JP H3193839 A **[0015]**
- JP H3199330 A **[0015]**

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- **TOMOKI SHIBATA** ; **NOBORU DEMIZU**. Deoxidation of TiAl. *Electric Steelmaking*, February 1993, vol. 64 (1), 32-39 **[0016]**