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(72) Inventors:

- **TAMURA, Keitaro**
Hyogo 676-8670 (JP)
- **ITSUMI, Yoshio**
Hyogo 676-8670 (JP)
- **MATSUKURA, Norikazu**
Tokyo 141-8688 (JP)
- **SUZUKI, Jun**
Hyogo 651-2271 (JP)

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(71) Applicant: **Kabushiki Kaisha Kobe Seiko Sho**
(Kobe Steel, Ltd.)
Kobe-shi, Hyogo 651-8585 (JP)

(74) Representative: **Müller-Boré & Partner**

Patentanwälte PartG mbB
Friedenheimer Brücke 21
80639 München (DE)

(54) **TITANIUM ALLOY SHEET FOR ELECTRODE**

(57) Disclosed is a titanium alloy sheet for electrode, including at least one of 0.1 to 1.0% by mass of Al and 0.1 to 1.0% by mass of Si, with the balance being Ti and inevitable impurities, wherein the total content of Al and Si is 0.2 to 1.0% by mass and an average grain size is 5 to 20 μm .

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Description

Technical Field

[0001] The present disclosure relates to a titanium alloy sheet for electrode, that is used for an electrode of an electrolytic cell in electrolysis such as soda electrolysis, water electrolysis, or industrial electrolysis accompanied by generation of oxygen, chlorine or the like.

Background Art

[0002] In various electrolytic processes including soda electrolysis for producing sodium hydroxide, chlorine gas and hydrogen gas by electrolysis of an aqueous sodium chloride solution, an anode using titanium as a base material has been widely used. Specifically, there has been used an electrode material for anode in which a base material made of pure titanium (titanium sheet) is processed into a shape having many holes, such as an expanded metal or a punched perforated sheet, and then an electrode catalyst layer containing an electrode catalyst component composed of platinum group metal and an oxide thereof is formed on a surface thereof.

[0003] When pure titanium is used as the base material, an oxide film existing between a surface of pure titanium and the electrode catalyst layer acts as a resistance, thus degrading electrolysis efficiency. If this electric resistance can be reduced, the electrolysis efficiency can be improved, thus enabling reduction in electricity consumption and reduction in costs.

[0004] Patent Document 1 discloses an anode capable of improving properties such as energy consumption by using, as a base material, a titanium alloy containing at least one element selected from the first group consisting of aluminum, niobium, chromium, manganese, molybdenum, ruthenium, tin, tantalum, vanadium and zirconium and at least one element selected from the second group consisting of nickel, cobalt, iron and copper, and palladium.

[0005] Patent Document 2 discloses a method for producing an electrode for electrolysis in which performances of the electrode are not degraded even if the amount of an electrode catalyst component used is decreased by using a base material containing at least one metal selected from titanium, tantalum, niobium, zirconium, hafnium and nickel or an alloy thereof, and an electrode catalyst component with a predetermined composition, and applying the electrode catalyst component under predetermined conditions. Conventional Art Document

Patent Document

[0006]

Patent Document 1: JP 5616633 B1
Patent Document 2: JP 5548296 B1

Disclosure of the Invention

Problems to be Solved by the Invention

[0007] However, even if the electrodes (anodes) mentioned in Patent Documents 1 and 2 are used, the electrolytic efficiency may not be sufficient.

[0008] The embodiment of the present invention has been made in view of the foregoing circumstances, and it is an object thereof to provide a sheet material for electrode, that can be used as a base material for electrode and enables reduction in electric resistance when an electrode catalyst layer is formed on a surface, thus enabling realization of high electrolysis efficiency of an electrode using this base material.

Means for Solving the Problems

[0009] The titanium alloy sheet for electrode according to the embodiment of the present invention can be used as a base material for electrode. The titanium alloy sheet for electrode is a titanium alloy sheet including at least one of 0.1 to 1.0% by mass of Al and 0.1 to 1.0% by mass of Si, the total content of Al and Si being 0.2 to 1.0% by mass, wherein the balance is composed of Ti and inevitable impurities and an average grain size is 5 to 20 μm .

[0010] It is preferred that the titanium alloy substrate for electrode according to the embodiment of the present invention has an oxide film containing at least one of Al and Si on a surface thereof, and the total content of Al and Si in the oxide film is 0.08 to 0.55% by mass.

Effects of the Invention

[0011] The titanium alloy sheet for electrode according to the embodiment of the present invention can be used as a base material for electrode and enables reduction in electric resistance when an electrode catalyst layer is formed on a surface thereof. Therefore, when using for an electrode, high electrolysis efficiency can be obtained.

Mode for Carrying Out the Invention

[0012] Since titanium is metal having extremely high activity, even if an oxide film existing on a surface of pure titanium or a titanium alloy sheet is removed, new oxide film is immediately formed. Therefore, when pure titanium or a titanium alloy is used as a base material and an electrode is produced by providing an electrode catalyst layer on a surface thereof, it is difficult to avoid that an oxide film is interposed between the metal portion of the pure titanium or titanium alloy of the base material and a contact layer.

[0013] In view of such circumstances, the inventors of the present invention have intensively studied a method of reducing electric resistance (e.g., contact resistance) between a base material and an electrode catalyst layer when the electrode catalyst layer is formed on a surface of the base material, on the premise that an oxide film exists on a surface of the base material.

[0014] As a result, as will be mentioned in detail below, it has been found that when using, as a base material, a titanium alloy sheet including at least one of 0.1 to 1.0% by mass of Al and 0.1 to 1.0% by mass of Si, the total of the Al content and the Si content being 0.2 to 1.0% by mass in which an average grain size is 5 to 20 μm , and an electrode catalyst layer is formed thereon, the electrical resistance can be reduced, thus completing the embodiment of the present invention.

[0015] By controlling the composition and the average grain size in this way, a certain amount of at least one of Al and Si exists in an oxide film formed on a surface, thus making it possible to suppress the growth of the oxide film and improving the adhesion between the oxide film and the electrode catalyst layer, leading to reduction in electric resistance.

[0016] Therefore, the total content of Al and Si in the oxide film is preferably 0.08 to 0.55% by mass.

[0017] The titanium alloy sheet for electrode according to the embodiment of the present invention will be described in detail below.

[0018] As mentioned above, an oxide film is inevitably formed on the surface of the titanium alloy. Accordingly, the term "titanium alloy sheet" as used herein is a concept including the embodiment in which an oxide film is formed on the surface. In principle, the composition mentioned below is the composition of the metal portion excluding the oxide film on the surface. However, since the oxide film is formed within a short time even if it is removed as mentioned above, it is often difficult to complete composition analysis in a state where the oxide film is removed. The thickness of the oxide film formed on the surface is, for example, about 20 nm or less, and the amount of the oxide film is overwhelmingly smaller than that of the metal portion. Therefore, the results of composition analysis performed using a bulk sample with an oxide film formed thereon may be regarded as the composition of a titanium alloy sheet. For example, it is possible to use a method that is generally used for composition analysis such as ICP emission spectroscopy.

[0019] When the composition of raw materials used for blending is clear, values calculated from the composition of raw materials and amounts may be used.

1. Composition

[0020] In order to contain at least one of Al and Si in an oxide film, the titanium alloy sheet for electrode according to the embodiment of the present invention includes at least one of 0.1 to 1.0% by mass of Al and 0.1 to 1.0% by mass of Si. The total content of Al and Si is 0.2 to 1.0% by mass. In the case of including only Al, the content of Al becomes 0.2% by mass or more in order to satisfy 0.2% by mass that is the lower limit of the total content of Al and Si. In the case of including only Si, the Si content becomes 0.2% by mass or more in order to satisfy 0.2% by mass that is the lower limit of the total content of Al and Si. The balance is composed of Ti and inevitable impurities.

[0021] If the Al content is less than 0.1% by mass, sufficient Al does not exist in the oxide film, and it is impossible to sufficiently obtain the effect of suppressing the growth of the oxide film and improving the adhesion to the electrode catalyst layer by Al. If the Si content is less than 0.1% by mass, sufficient Si does not exist in the oxide film, and it is impossible to sufficiently obtain the effect of suppressing the growth of the oxide film and improving the adhesion to the electrode catalyst layer by Si.

[0022] In order to sufficiently obtain the effect of suppressing the growth of the oxide film and improving the adhesiveness with the electrode catalyst layer, it is possible to sufficiently include at least one of Al and Si in the oxide film by containing Al and Si in the total content of 0.2% by mass or more. This makes it possible to reduce the electric resistance and to improve the electrolysis efficiency.

[0023] It is possible to exemplify, as the electrode catalyst layer, a layer made of a platinum group metal and/or an

oxide thereof.

[0024] Meanwhile, if the Al content exceeds 1.0% by mass or the Si content exceeds 1.0% by mass, or the total of the Si content and the Al content exceeds 1.0% by mass, the hardness increases, thus degrading the processability. The titanium alloy sheet for electrode is usually used after being processed into a shape having many holes, such as an expanded metal or a punched perforated sheet. However, it becomes difficult to process into such a shape.

[0025] Preferably, the titanium alloy sheet for electrode includes at least one of 0.3 to 0.5% by mass of Al and 0.3 to 0.5% by mass of Si, and the total content of Al and Si is 0.6 to 0.9% by mass.

2. Grain Size

[0026] The titanium alloy substrate for electrode according to the embodiment of the present invention has an average grain size of 5 μm or more and 20 μm or less.

[0027] By setting the average grain size at 20 μm or less, it is possible to improve the adhesion between the oxide film on the surface and the electrode catalyst layer. One reason is that the surface roughness tends to decrease if the average grain size is 20 μm or less. In addition to this, the other reason is that, by setting the average grain size at 20 μm or less, at least one of Al and Si can be contained in the oxide film in the greater amount even with the same composition.

[0028] Si and Al tend to be easily concentrated in grain boundaries. When an oxide film is formed, Si and Al in grains do not enter the oxide film but to be expelled to the metal portion. Meanwhile, Si and Al in the grain boundary tend to be incorporated into the oxide film. Therefore, by decreasing the average grain size thereby increasing the grain boundary and concentrating a greater amount of Si and Al in the grain boundary, a sufficient amount of Si and/or Al can be contained in the oxide film, thus enabling an improvement in adhesion between the oxide film and the electrode catalyst layer. Containing a sufficient amount of Si and/or Al in the oxide film also has the effect of suppressing the growth of the oxide film. This makes it possible to reduce the electric resistance and to improve the electrolysis efficiency.

[0029] If the average grain size exceeds 20 μm , it is impossible to sufficiently obtain the above-mentioned effect of improving the adhesion. Meanwhile, if the average grain size is less than 5 μm , the hardness increases, thus degrading the processability. The titanium alloy sheet for electrode is usually used after being processed into a shape having many holes, such as an expanded metal or a punched perforated sheet. However, it becomes difficult to process into such a shape.

[0030] The average grain size is preferably 10 μm or more and 15 μm or less.

[0031] The average grain size can be determined by a section method using the results of structure observation with an optical microscope.

3. Al Content and Si Content in Oxide Film

[0032] By setting at the above-mentioned composition and average grain size, a sufficient amount of at least one of Al and Si can be contained in the oxide film. This makes it possible to improve the adhesion between the oxide film and the electrode catalyst layer. As a result, the electric resistance between the base material and the electrode catalyst layer can be reduced, thus enabling an improvement in electrolysis efficiency.

[0033] The oxide film formed on the surface of the titanium alloy sheet according to the embodiment of the present invention preferably contains at least one of Al and Si, and the total content of Al and Si is 0.08 to 0.55% by mass.

[0034] When the oxide film contains Al and does not contain Si, the content of Al in the oxide film is preferably 0.08 to 0.55% by mass. When the oxide film contains Si and does not contain Al, the content of Si in the oxide film is preferably 0.08 to 0.55% by mass. When the oxide film contains Al and Si, the total content of Al and Si in the oxide film is preferably 0.08 to 0.55% by mass. This makes it possible to more surely obtain the effect of suppressing the growth of the oxide film and the effect of improving the adhesion between the oxide film and the electrode catalyst layer. As a result, it is possible to more surely reduce the electrical resistance between the base material and the electrode catalyst layer, thus enabling an improvement in electrolysis efficiency.

[0035] If the total content of Al and Si is more than 0.55% by mass, the hardness of the oxide film may increase and the abrasion of the tool or the like may be accelerated in the case of processing into a shape having many holes, such as an expanded metal or a punched perforated sheet. Therefore, the total content of Al and Si is preferably 0.55% by mass or less.

[0036] More preferably, the oxide film contains at least one of Al and Si, and the total content of Al and Si is 0.10 to 0.40% by mass.

[0037] The Al content and the Si content in the oxide film can be measured by performing composition analysis using EDS attached to TEM during TEM observation.

4. Method for Producing Titanium Alloy Sheet for Electrode

[0038] The method for producing a titanium alloy sheet for electrode according to the embodiment of the present invention will be described below.

[0039] A cast billet such as bloom or slab with a desired composition is obtained by melting and forging as needed. It is possible to use a method that is commonly used for melting a titanium alloy, such as VAR (vacuum arc remelting). A small amount of a sample may be obtained by button arc melting or the like.

[0040] The thus obtained cast billet such as bloom or slab is heated to 750°C to 850°C and then subjected to hot-rolling to obtain a hot-rolled sheet. Heating may be performed in the atmosphere, for example, by open flame of burners disposed in upper and lower portions of a heating furnace. As an example of the finish thickness of hot-rolling, 3 mm to 5 mm can be exemplified.

[0041] Subsequently, annealing is performed to remove processing strain. In the sheet material after annealing, oxidation scale and an oxygen diffusion layer exist on the surface due to heating of hot-rolling and annealing. If the oxidation scale and the oxygen diffusion layer remain, the electric resistance increases, thus degrading the electrolysis efficiency when used as an electrode. During cold-rolling, they can cause flaws. Therefore, there is a need to remove the oxide scale and oxygen diffusion layer. For example, they can be removed by pickling.

[0042] The thickness (total thickness) L (m) of the oxidation scale and oxygen diffusion layer depends on the heating temperature T (K) and the heating time t (second) and can be determined by the following equation (1):

$$L = 2 (Dt)^{0.5} \quad (1)$$

where $D = D_0 \times \exp(-Q/(RT))$, diffusion coefficient $D_0 = 5.08 \times 10^{-7}$ m²/second, activation energy $Q = 140$ kJ/mol, and gas constant $R = 8.3144$.

[0043] Therefore, when the oxidation scale and the oxygen diffusion layer are removed by pickling or the like, the removal amount (pickling amount) are required to exceed L . Pickling can be performed using fluonitric acid or the like.

[0044] After removing the amount exceeding L from the surface by pickling or the like, the hot-rolled sheet is rolled to a predetermined thickness by a cold-rolling step.

[0045] After the cold-rolling, in order to remove processing strain similar to the case after the hot-rolling step, the cold-rolled sheet is placed in a furnace to conduct an annealing treatment in the atmosphere. By setting the heating temperature at this time to 780 to 830°C, it is possible to control the average grain size within a predetermined range.

[0046] Since the oxidation scale and oxygen diffusion layer exist on the surface of the sheet material even after the cold-rolling and subsequent annealing, the thickness L of the oxidation scale and oxygen diffusion layer is determined by the equation (1), and the surface is removed by pickling or the like by the amount exceeding L thus obtained. Pickling can be performed using fluonitric acid or the like.

[0047] Since titanium is metal that is active with oxygen, an oxide film is formed on a surface of a titanium alloy sheet immediately after pickling. During the formation of the oxide film, Al and Si existing near the surface are incorporated into the oxide film. When the oxygen diffusion layer exists near the surface because of insufficient pickling, Al and Si are hardly incorporated into the oxide film due to interference of oxygen, thus failing to contain a sufficient amount of Al and/or Si in the oxide film.

[0048] Therefore, there is a need to surely remove the surface by the amount (thickness) of L or more determined by the equation (1) by pickling or the like.

[0049] Thus, the titanium alloy sheet for electrode according to the embodiment of the present invention can be obtained.

Examples

1. Fabrication of Test Materials

[0050] The present invention will be described in more detail by way of the following Examples. It should be noted that the following Embodiments are intended to facilitate understanding of the present invention and do not limit the scope of the present invention.

[0051] Test materials were fabricated in the following way.

[0052] Ingot of titanium alloys with each composition shown in Table and having a size of about 40 mm in diameter $\times$ 20 mm in height was manufactured using button arc melting.

[0053] The ingot was heated to 1,000°C and subjected to forging to fabricate the forged material with a size of 10 mm in thickness $\times$ 35 mm in width $\times$ 75 mm in length. After surface grinding and heating at 850°C for 120 minutes, hot-rolling was performed to obtain a sheet with a size of 3.5 mm in thickness $\times$ 35 mm in width $\times$ 165 mm in length.

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Thereafter, annealing at 750°C for 20 minutes was performed in the atmosphere.

[0054] Then, the sheet thus obtained was pickled with fluonitric acid. Each thickness L of an oxidation scale and an oxygen diffusion layer determined by the equation (1) was about 80 μm . In order to surely remove the oxide scale and oxygen diffusion layer, the removal amount (pickling amount) by pickling was set at 120 μm on one side (240 μm on both sides).

[0055] Subsequently, cold-rolling was performed at room temperature to obtain a sheet with a size of 0.52 mm in thickness, 36 mm in width $\times$ 1,000 mm in length.

[0056] Then, this sheet was annealed in the atmosphere at 800°C for 2 minutes.

[0057] Then, the sheet was pickled with fluonitric acid. Each thickness L of an oxidation scale and an oxygen diffusion layer determined by the equation (1) was about 6 μm . In order to surely remove the oxide scale and the oxygen diffusion layer, the removal amount (pickling amount) by pickling was set at 10 μm on one side (20 μm on both sides).

2. Evaluation Results of Test Materials

[0058] The test material thus obtained was cut into a predetermined size and cross-sectional observation (at a magnification of 100,000 times) was performed using a transmission electron microscope (TEM). Using the thus obtained micrograph (TEM image), after selecting five positions where the thickness of the oxide film is considered to be representative, the thickness of the oxide film in this point was measured and the average thereof was taken as the thickness of the oxide film. The results are shown in Table 1.

[0059] Quantitative analysis with EDS was also performed and the component values near the center in the thickness direction of the oxide film were measured at five positions randomly selected, and then each content of Al and Si in the oxide film was determined from the average. The results are shown in Table 1.

[0060] The average grain size was measured at one field of view having an area of 520 $\mu\text{m} \times 860 \mu\text{m}$ by a section method using the results of structure observation with an optical microscope (at a magnification of 100 times). The results are shown in Table 1.

[0061] Vickers hardness (load of 10 kgf) was measured at five positions near the center in the thickness direction of the cross section and the average was taken as hardness. The results are shown in Table 1.

[Table 1]

	Alloy composition (% by mass)			Thickness of oxide film (nm)	Component in oxide film (% by mass)		Average grain size (μm)	Hardness Hv	Contact resistance ($\text{m}\Omega \cdot \text{cm}^2$)
	Al	Si	Ti		Al	Si			
Example 1	0.10	0.00	Bal.	7.32	0.08	0.00	18.6	147	4.5
Example 2	0.30	0.00	Bal.	7.15	0.18	0.00	15.4	150	5.5
Example 3	0.50	0.00	Bal.	6.80	0.25	0.00	11.6	183	4.0
Example 4	1.00	0.00	Bal.	6.78	0.28	0.00	9.6	199	3.1
Example 5	0.00	0.50	Bal.	6.73	0.00	0.50	5.1	199	4.1
Example 6	0.00	1.00	Bal.	6.69	0.00	0.53	5.0	199	3.6
Example 7	0.50	0.35	Bal.	6.80	0.24	0.25	7.9	192	4.0
Comparative Example 1	0.00	0.00	Bal.	7.71	0.00	0.00	36.2	144	6.5
Comparative Example 2	1.50	0.00	Bal.	6.77	0.35	0.00	10.5	225	-
Comparative Example 3	0.00	1.50	Bal.	6.65	0.00	0.58	4.3	214	-

[0062] As is apparent from Table 1, the test materials of Examples 1 to 7 and Comparative Example 1 exhibit hardness (Hv) of less than 200 and have excellent processability. Meanwhile, the test material with excess Si content of Comparative Example 2 and the test material with excess Al content of Comparative Example 3 exhibit hardness of 200 or more and have insufficient processability.

3. Measurement of Contact Resistance

[0063] With respect to the test materials in which processability was rated good because of having hardness of 200 or less of Examples 1 to 7 and Comparative Example 1, an electrode catalyst layer was formed on a surface and the contact resistance was measured.

[0064] After shot blasting and pickling, the above-mentioned test material was cut into a size of 20 mm in width $\times$ 40 mm in length and an electrode catalyst layer was formed on both sides. Specifically, a catalyst layer-forming solution prepared by mixing a ruthenium chloride acid solution, an iridium chloride acid solution and titanium chloride was applied to a surface of each sample after subjecting to shot blasting and pickling, placed in a dryer (inside temperature: 75°C) and dried for 2 minutes. The dried sample was placed in an atmosphere heat treatment furnace set at a furnace temperature of 475°C, held for 10 minutes and then taken out. Lamination was performed by repeating the operation from application of the catalyst layer-forming solution to heat treatment (holding) five times. Finally, a heat treatment was performed at 500°C for 60 minutes to form an electrode catalyst layer.

[0065] The contact resistance of the sample on which the electrode catalyst layer was formed was measured.

[0066] The sample after formation of the catalyst layer was interposed between gold sheets, and two gold sheets between which the sample was interposed was further interposed between two copper electrodes under a load of 10 kgf so that the contact area became 1 cm². In this state, a current was applied between two copper electrodes and the voltage at that time was measured by a voltmeter disposed between two gold sheets. The contact resistance was determined from the current applied and the measured voltage.

[0067] The results are shown in Table 1. All the samples of Examples 1 to 7 exhibit low contact resistance of 3.1 to 5.5 m Ω ·cm² and can realize high electrolysis efficiency. Meanwhile, the sample with insufficient Si and Al contents and excess average grain size of Comparative Example 1 exhibits large contact resistance of contact resistance of 6.5 m Ω ·cm².

[0068] This application claims priority based on Japanese Patent Application 2016-163915 filed on August 24, 2016, the disclosure of which is incorporated by reference herein.

Claims

1. A titanium alloy sheet for electrode, comprising at least one of 0.1 to 1.0% by mass of Al and 0.1 to 1.0% by mass of Si, with the balance being Ti and inevitable impurities, wherein the total content of Al and Si is 0.2 to 1.0% by mass and an average grain size is 5 to 20 μ m.
2. The titanium alloy sheet for electrode according to claim 1, which has an oxide film containing at least one of Al and Si on a surface thereof and the total content of Al and Si in the oxide film is 0.08 to 0.55% by mass.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2017/029820

A. CLASSIFICATION OF SUBJECT MATTER

C22C14/00(2006.01)i, C22F1/18(2006.01)i, C25B11/10(2006.01)i, C22F1/00(2006.01)n

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)
C22C14/00, C22F1/18, C25B11/10, C22F1/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2017
Kokai Jitsuyo Shinan Koho 1971-2017 Toroku Jitsuyo Shinan Koho 1994-2017

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 2013-007063 A (Nippon Steel & Sumitomo Metal Corp.), 10 January 2013 (10.01.2013), claims; paragraphs [0001] to [0002], [0024]; tables 1 to 3 (Family: none)	1 2
A	JP 2011-195884 A (Kobe Steel, Ltd.), 06 October 2011 (06.10.2011), (Family: none)	1-2

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search
12 September 2017 (12.09.17)

Date of mailing of the international search report
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Patent documents cited in the description

- JP 5616633 B [0006]
- JP 5548296 B [0006]
- JP 2016163915 A [0068]