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DESCRIPTION

ALUMINUM NITRIDE SINTERED BODY AND
PROCESS FOR PRODUCING THE SAME

TECHNICAL FIELD

The present invention relates to an aluminum
5 nitride sintered body and a process for producing the
same, in particular to an aluminum nitride sintered
body which is black and has a high heat conductivity.

BACKGROUND ART

In recent years, the technical advance of a
10 large scale integrated circuit (LSI) device is
significant and, in particular, an improvement in the
integration density is remarkable. With an
improvement in the integration density, the size of
the IC chip has been increased and the density of the
15 wiring per IC chip has been increased. This has led
to a remarkable increase in the heat build up per IC
chip. For this reason, great importance has come to
be placed on the heat radiating property of a material
constituting a package on which IC chips are mounted.
20 An alumina sintered body has hitherto found extensive
use as the material of an IC chip substrate. With the
heat conductivity of the alumina sintered body,
however, it is becoming difficult to ensure a heat
radiating property sufficient to cope with an increase
25 in the heat buildup of the IC chip. Studies have been
made also on the use of a beryllium oxide sintered
body having a high heat conductivity as an alternative
to the alumina sintered body. The beryllium oxide is,

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however, difficult to handle due to the toxicity of the material per se and therefore can be used for a special application only.

On the other hand, an aluminum nitride sintered
5 body has a heat conductivity (theoretical value: 320 W/m·K) comparable with that of the beryllium oxide sintered body, is nontoxic and has a high insulating property. Therefore, it has attracted special interest recently in the field of semiconductor industries and
10 electronics including a high output laser, wherein the heat radiating property becomes an issue.

As described above, aluminum nitride is theoretically a material having a high heat conductivity and a high insulating property as a
15 single crystal. Since, however, aluminum nitride is a material having a covalent bond character of 50%, the diffusion coefficient of the constituent elements is small. Further, the sinterability of the aluminum nitride powder is much lower than that of the aluminum
20 oxide powder. Therefore, when a sintered body is produced from the aluminum nitride powder, the relative density (based on the theoretical density of aluminum nitride, that is, 3.26 g/cm^3) of the aluminum nitride sintered body produced by powder molding
25 followed by sintering is as low as 70 to 80% although it depends upon the sintering conditions, and the sintered body has a large amount of pores.

On the other hand, the heat conduction of the aluminum nitride sintered body having an insulating
30 property occurs through the movement of phonons as pseudo-particles. For this reason, defects such as pores or impurities in the crystal lattice cause scattering of phonons, which brings about a lowering in the heat conductivity of the aluminum nitride



sintered body.

Under these circumstances, various proposals have been made for the purpose of producing an aluminum nitride sintered body having a high conductivity.

In order to produce an aluminum nitride sintered body having a high conductivity, however, it is necessary to use a starting material having a high purity and to prevent the contamination with impurities in the manufacturing process. The resultant aluminum nitride sintered body is limited to a white or thinly colored sintered body, which renders the sintered body unusable in applications where the transmission of light becomes a problem. For this reason, the development of a colored aluminum nitride sintered body has been desired in such applications.

The present inventors have already proposed a highly heat conductive aluminum nitride sintered body having a light shielding property in Japanese Patent Laid-Open No. 124772/1990.

In the conventional light shielding aluminum nitride sintered body, the light shielding property is obtained by distributing a transition metal compound in the sintered body and allowing the light to be absorbed or diffused in the compound. No properties of the aluminum nitride sintered body, such as heat conductivity, can be sufficiently obtained depending upon the type of the transition metal added. This appears to derive from the fact that the transition metal compound in the aluminum nitride sintered body is not sufficiently controlled.

Accordingly, an object of the present invention is to eliminate the above-described problem and, at the same time, to provide an aluminum nitride sintered



body stabilized in the properties such as light shielding property and heat conductivity and a process for producing the same.

DISCLOSURE OF THE INVENTION

5 The present inventors have made detailed studies on an aluminum nitride sintered body and, as a result, have found that particularly the addition of a titanium compound as a means for stabilizing the heat conductivity and meeting the light shielding property
10 requirement serves to stabilize both the light shielding property and the heat conductivity.

 Accordingly, the present invention relates to an aluminum nitride sintered body characterized by comprising aluminum nitride as the main component,
15 containing a titanium compound, and having a black color, a transmittance of 10% or less with the light having a wavelength in the range of from 500 to 650 nm and a heat conductivity of 120 W/m·K or more.

 The titanium compound includes Ti_nO_{2n-1} or a
20 solid solution comprising Ti_nO_{2n-1} and nitrogen partly dissolved therein in the solid solution form wherein n is 1 or more. The n value may vary widely. When n is 1, the titanium compound is TiO and, for example, when n is 10, it is $Ti_{10}O_{19}$. The object of the present
25 invention can be attained so far as the titanium compound is none of TiN , Ti_2O_3 and TiO_2 . It is conceivable that the Ti_nO_{2n-1} may contain nitrogen in a solid solution form. However, it is difficult to determine the amount of such nitrogen by analysis.

30 The content of Ti_nO_{2n-1} in aluminum nitride is 0.05 to 5.0% by weight, preferably 0.05 to 1.0% by weight, in terms of Ti. When the content is less than



0.05% by weight, the light shielding property is unsatisfactory. On the other hand, when it exceeds 5.0% by weight, the insulating property deteriorates.

Further, the titanium compound includes a
5 compound represented by the formula TiN_xO_y wherein $0 < x < 1$ and y is $3/2 \cdot (1 - x)$. It is possible that the y value varies widely. When the x value is 0.95, the compound is $TiN_{0.95}O_{0.075}$. The X-ray diffractometry of TiN_xO_y comprising TiN and oxygen dissolved therein
10 in the form of a solid solution reveals that the titanium compound has a TiN crystalline structure. The amount of oxygen in the solid solution form is determined by estimating the bond energy of elementary titanium according to ESCA (X-ray photoelectron
15 spectroscopy) to simultaneously determine two kinds of bonding states, that is, the energy of bonding between a titanium atom and an oxygen atom of 459 and 465 eV (± 1 eV) and the energy of bonding between a titanium atom and a nitrogen atom of 456 and 462 eV (± 1 eV).

20 The content of the Ti-N-O compound in the aluminum nitride powder or aluminum nitride sintered body is 0.05 to 5.0% by weight in terms of Ti. When the content is less than 0.05% by weight, the shielding property of the aluminum nitride sintered
25 body is unsatisfactory, while when it exceeds 5.0% by weight, the insulating property of the aluminum nitride sintered body deteriorates.

According to a preferred embodiment of the aluminum nitride sintered body of the present
30 invention, the sintered body has a linear transmittance of 5% or less with the light having a wavelength of 500 nm or a linear transmittance of 10% or less with the light having a wavelength of 6.0 μm and a heat conductivity of 120 W/m·K or more in terms



of a sample thickness of 0.5 mm.

The present invention also provides a process for producing an aluminum nitride sintered body characterized by adding 0.05 to 5% by weight, in terms
5 of Ti, of a titanium compound and a sintering aid to an aluminum nitride powder, molding the mixture, heating the molding in vacuo, air, a nitrogen gas, a hydrogen gas or an atmosphere comprising a mixture of these gases until the residual carbon content is
10 reduced to 0.2% by weight or less, and sintering the heat-treated mixture in a nonoxidizing atmosphere containing nitrogen at 1600°C or above.

Further, the present invention provides a process for producing an aluminum nitride sintered
15 body characterized by adding 0.05 to 5% by weight, in terms of Ti element, of a titanium compound, a compound capable of forming carbon after being thermally decomposed and a sintering aid to an aluminum nitride powder, molding the mixture, heating
20 the molding in vacuo, air, a nitrogen gas, a hydrogen gas or an atmosphere comprising a mixture of these gases until the residual carbon content is reduced to 0.2 to 2.0% by weight, and sintering the heat-treated mixture in a nonoxidizing atmosphere containing
25 nitrogen at 1600°C or above.

In the process according to the present invention, it is preferred to use an aluminum nitride powder having a high purity. For example, it is preferred that the absorption peak of aluminum nitride
30 (wherein aluminum is coordinated with four nitrogen atoms) obtained by an infrared absorption method using KBr be observed at 750 cm^{-1} or less. In particular, in the aluminum nitride powder, the amount of oxygen, carbon, etc., in the solid solution form in the



aluminum nitride powder particle and the amount of metallic elements as impurities included in the powder should be small.

5 The titanium compound to be added to the aluminum nitride powder should be convertible into metallic titanium, TiO or TiO_2 when heated. Preferred examples of such a compound include organometallic compounds, metal alkoxide compounds and stearates. The amount of addition of the titanium compound is
10 still preferably in the range of from 0.05 to 5.0% by weight in terms of Ti for the reasons as described above. The titanium compound to be added may also be TiO_2 (having a rutile crystal structure) comprising ultrafine particles having a primary particle diameter
15 of 500 nm or less.

At least one compound selected among those of rare earth elements and alkaline earth elements is used as the sintering aid. The amount of addition of the sintering aid is preferably in the range of from
20 0.01 to 10.0% by weight in terms of oxide. The addition of the sintering aid facilitates the production of an aluminum nitride sintered body having a high density, so that the object of the present invention can be attained.

25 The above-described starting materials are mixed together and molded, and the resultant molding is heated at 200 to 1000°C in the air, vacuo, a nitrogen gas, a hydrogen gas or an atmosphere comprising a mixture of these gases. The content of the residual
30 carbon is regulated by either adding a compound capable of forming carbon after being thermally decomposed or not. In this case, the reason why the heating atmosphere is limited as described above resides in that the aluminum nitride powder suffers no



significant oxidation and the residual carbon content can be regulated thereby. The term "residual carbon" used herein is intended to mean liberated carbon. The residual carbon content is limited to 2.0% by weight or less because when the content exceeds 2.0% by weight, TiN and TiC are formed and besides the relative density of the aluminum nitride sintered body is reduced to 90% or less.

The molding thus treated is sintered at a temperature of 1600°C or above in a nonoxidizing atmosphere containing nitrogen.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a graph showing the results of measurement of the linear transmittance of an aluminum nitride sintered body prepared in Example 3, and FIG. 2 is a graph showing the results of the ESCA analysis of an aluminum nitride sintered body prepared in Example 3.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will now be described in more detail with reference to the following Examples.

Example 1:

An Y_2O_3 powder (particle diameter: 0.5 μm) and a titanium compound of the type and in an amount as specified in Table 1 were added to an AlN powder having an average particle diameter of 0.8 μm (oxygen: 1.5%, carbon: 0.03%, metal impurities: 0.1% or less in total). They were mixed with each other in alcohol, dried and molded on a dry press to prepare moldings each having a diameter of 15 mm and a thickness of 3



mm. The moldings were heated in the air at 400°C for 30 min to remove the binder, and sintered in a nitrogen gas flow under sintering conditions specified in the Table 1. The properties of the resultant sintered bodies are also given therein. As is apparent from the table, according to the present invention, it is possible to produce an AlN sintered body having an excellent shielding property and a high heat conductivity.

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Table 1:

No.	Y ₂ O ₃ amt. of addition	Ti compd.	Amount of addition wt. % (in terms of Ti)	Sintering conditions (°C x H)	Ti compd. (according to TEM)	Properties of sintered body	
						heat conductivity (W/m.K)	transmittance (%)
*1	3.0%	Ti alkoxide	0.01	1850°Cx3H	TiO	180	15
2	do.	do.	0.07	do.	TiO	170	4
3	do.	do.	0.20	do.	TiO	170	2
4	do.	do.	0.70	do.	TiO	170	1
5	do.	do.	2.0	do.	TiO	160	1
6	do.	Ti stearate	0.5	do.	TiO	170	1
7	1.0	do.	do.	do.	TiO	170	1
8	0.5	do.	do.	do.	TiO	170	1
9	7.0	do.	do.	do.	TiO	180	1
10	1.0	do.	do.	1750°Cx3H	TiO	170	1

Note: * Comparative Example

Example 2:

5 A titanium compound in an amount of 0.2% by weight in terms of Ti and a sintering aid listed in Table 2 were added to an AlN powder having an average particle diameter of 0.8 μ m (oxygen: 1.5%, carbon: 0.03%, metal impurities: 0.1% or less in total). They were sufficiently mixed with each other in alcohol, dried and molded on a simple spindle press to prepare moldings each having a diameter of 15 mm and a
10 thickness of 3 mm. The moldings were heated in a steam stream at 700°C for 30 min to remove the binder, and sintered in a nitrogen gas flow under sintering conditions specified in the Table 2. The properties of the resultant sintered bodies are also given
15 therein.

As is apparent from the table, according to the present invention, it is possible to produce an AlN sintered body having an excellent shielding property and a high heat conductivity.

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Table 2:

No.	Sintering aid	Amt. of addition wt%	Ti compd.	Sintering conditions ($^{\circ}\text{C} \times \text{H}$)	Ti compd.	Properties of sintered body	
						heat conductivity ($\text{W/m}\cdot\text{K}$)	transmittance (%)
11	CaO	2.0	TiCO_3	$1800^{\circ}\text{C} \times 3\text{H}$	TiO	130	1
12	CaO	0.8	TiCO_3	do.	TiO	130	1
13	CaO Y_2O_3	0.8 1.5	TiO_2	do.	TiO	150	1
14	Gd_2O_3	1.5	TiO_2	do.	TiO	130	1
15	$\text{Y}(\text{NO}_3)_3$	1.5	TiO_2	do.	TiO	140	1

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Example 3:

A Y_2O_3 powder (particle diameter: $0.5\ \mu m$) and titanium stearate in an amount of 0.3% by weight in terms of titanium were added to an aluminum nitride powder having an average particle diameter of $1.5\ \mu m$ (oxygen content: 1.5% by weight, carbon content: 0.04% by weight, content of metal impurities: 0.1% by weight or less). 11% by weight of an organic binder for molding was added to the mixed powder, and they were mixed with each other in a combined solvent comprising toluene and alcohol. The organic binder used was a mixture of polyvinyl butyral (PVB) with dibutyl phthalate (DBP) in a ratio of 6 : 4. Thereafter, the mixture was molded by the doctor blade method into a sheet having a thickness of 0.8 mm. The molding was heated in a nitrogen atmosphere at $600^\circ C$ for 2 hr to remove the organic binder component. Thereafter, the molding was sintered in a nitrogen gas atmosphere having a CO gas concentration of 200 ppm or less at $1850^\circ C$ for 1 hr.

The resultant aluminum nitride sintered body was molded into a sheet having a thickness of 0.5 ± 0.01 mm and subjected to measurement of the linear transmittance with FT-IR7000, manufactured by Japan Spectroscopic Co., Ltd., and the heat conductivity with a thermal constant measuring device TC-3000, manufactured by Shinkuu-Rikoh Inc.

A sintered body wherein no titanium stearate had been added was prepared as a comparative sample under the same condition as that described above. The results of the measurement of the linear transmittance are shown in FIG. 1. The heat conductivity of the sintered body according to the example of the present invention was $185\ W/m \cdot K$, while that of the aluminum



nitride sintered body according to the comparative example was 183 W/m·K. As is apparent from the results, the aluminum nitride sintered body of the present invention is excellent in light shielding property and has a high heat conductivity.

FIG. 2 shows the results of the ESCA analysis of a sintered body wherein titanium stearate has been added. The figure shows the presence of bond energy levels of 456 eV, 459 eV, 462 eV and 465 eV. The bond energies of 459 eV and 465 eV refer to a bond between the titanium atom and the oxygen atom, while those of 456 and 462 eV refer to a bond between the titanium atom and the nitrogen atom.

Example 4:

A Y_2O_3 powder (average particle diameter: 0.5 μm), titanium stearate, a TiO_2 powder (average particle diameter: 100 Å) and a titanium alkoxide were added to an aluminum nitride powder having an average particle diameter of 1.5 μm (oxygen content: 1.5% by weight, carbon content: 0.04% by weight, content of metal impurities: 0.1% by weight or less). 11% by weight of an organic binder for molding was added to the mixed powder, and they were mixed with each other in a combined solvent comprising toluene and alcohol. The organic binder for molding used was a mixture of polyvinyl butyral (PVB) with dibutyl phthalate (DBP) in a ratio of 6 : 4. Thereafter, the mixture was molded by the doctor blade method into a sheet having a thickness of 0.8 mm. The molding was heated in a nitrogen atmosphere at 600 °C for 2 hr to remove the organic binder component. Thereafter, the molding thus obtained was sintered in a nitrogen gas flow atmosphere having a CO gas concentration of 200 ppm or less under various conditions specified in Table 3.



The resultant aluminum nitride sintered bodies were molded into sheets each having a thickness of 0.5 $\pm$ 0.01 mm and subjected to measurements of the linear transmittance with FT-IR7000, manufactured by Japan Spectroscopic Co., Ltd., and the heat conductivity with a thermal constant measuring device TC-3000, manufactured by Shinkuu-Rikoh Inc.

The results of the measurements are given in the Table 3, from which it can be understood that the sintered bodies of the present invention are excellent in light shielding property and have a high heat conductivity.

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Table 3:

No.	Y ₂ O ₃ amt. of addition wt. %	Ti compd.	Amt. of addition, wt. % (in terms of Ti)	Sintering conditions (°C x hr)	Ti compd. (according to ESCA)	Properties of sintered body	
						heat conductivity (W/m·K)	transmit- tance (%)
1	1.0	TiO ₂	0.01	1850°Cx2H	Ti-N-O	180	3.0
2	1.0	do.	0.05	do.	Ti-N-O	182	2.3
3	1.0	do.	0.10	do.	Ti-N-O	180	1.5
4	1.0	do.	0.50	do.	Ti-N-O	178	1.0
5	1.0	do.	1.0	do.	Ti-N-O	175	0.5
6	1.0	do.	5.0	do.	Ti-N-O	170	0.5
7	0.5	Ti alkoxide	0.5	1750 °Cx5H	Ti-N-O	150	1.0
8	0.5	do.	1.0	do.	Ti-N-O	155	0.6
9	1.0	do.	0.5	do.	Ti-N-O	158	0.9
10	1.0	do.	1.0	do.	Ti-N-O	157	0.7
11	5.0	do.	0.5	do.	Ti-N-O	166	1.0

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Table 3: (contd.)

No.	Y ₂ O ₃ amt. of addition wt. %	Ti compd.	Amt. of addition wt. % (in terms of Ti)	Sintering conditions (°C x H)	Ti compd. (according to ESCA)	Properties of sintered body	
						heat conductivity (W/mK)	transmit- tance (%)
12	5.0	Ti alkoxide	1.0	1750°C x 5H	Ti-N-O	164	1.1
13	0.5	Ti stearate	0.3	1800°C x 3H	Ti-N-O	193	1.2
14	0.5	do.	0.6	do.	Ti-N-O	195	0.8
15	1.0	do.	0.3	do.	Ti-N-O	225	1.4
16	1.0	Ti stearate	0.6	1800°C x 3H	Ti-N-O	201	0.7
17	3.0	do.	0.3	do.	Ti-N-O	197	1.1
18	3.0	Ti stearate	0.6	do.	Ti-N-O	189	0.6
19	5.0	do.	0.3	do.	Ti-N-O	210	1.0
20	5.0	-----	0.0	do.	-----	194	11

Note: No. 20 is a comparative example wherein no Ti compound has been added.

Example 5:

A CaO powder (average particle diameter: 1.5 μm), titanium stearate, a TiO_2 powder (average particle diameter: 100 $\text{\AA}$) and titanium alkoxide were added to an aluminum nitride powder having an average particle diameter of 1.5 μm (oxygen content: 1.4% by weight, carbon content: 0.07% by weight, content of impurities: 0.1% by weight or less). 11% by weight of an organic binder for molding was added to the mixed powder, and they were mixed with each other in a combined solvent comprising toluene and alcohol. The organic binder for molding used was a mixture of polyvinyl butyral (PVB) with dibutyl phthalate (DBP) in a ratio of 6 : 4. Thereafter, the mixture was molded by the doctor blade method into a sheet having a thickness of 0.8 mm. The molding was heated in a nitrogen atmosphere at 600°C for 2 hr to remove the organic binder component. Thereafter, the molding was sintered in a nitrogen gas flow atmosphere having a CO gas concentration of 200 ppm or less under various conditions specified in Table 4.

The resultant aluminum nitride sintered bodies were molded into sheets each having a thickness of 0.5 $\pm$ 0.01 mm and subjected to measurements of the linear transmittance with FT-IR7000, manufactured by Japan Spectroscopic Co., Ltd., and the heat conductivity with a thermal constant measuring device TC-3000, manufactured by Shinkuu-Rikoh Inc.

The results of the measurements are given in the Table 4, from which it can be understood that the sintered bodies of the present invention are excellent in light shielding property and have a high heat conductivity.

Table 4:

No.	CaO amt. of addition, wt. %	Ti compd.	Amt. of addition wt. % (in terms of Ti)	Sintering conditions (° C x H)	Ti compd. (according to ESCA)	Properties of sintered body	
						heat conductivity (W/m · K)	linear transmit- tance (%)
21	1.0	TiO ₂	0.01	1750°Cx3H	Ti-N-O	162	3.8
22	1.0	do.	0.05	do.	Ti-N-O	163	2.3
23	1.0	do.	0.10	do.	Ti-N-O	169	2.1
24	1.0	do.	0.50	do.	Ti-N-O	167	1.0
25	1.0	do.	1.0	do.	Ti-N-O	166	0.8
26	1.0	do.	5.0	do.	Ti-N-O	170	0.7
27	0.5	Ti alkoxide	0.5	1450°Cx5H	Ti-N-O	150	0.9
28	0.5	do.	1.0	do.	Ti-N-O	145	0.7

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Table 4: (contd.)

No.	CaO amt. of addition, wt. %	Ti compd.	Amt. of addition wt. % (in terms of Ti)	Sintering conditions (°C x H)	Ti compd. (according to ESCA)	Properties of sintered body	
						heat conductivity (W/m · K)	linear transmit- tance (%)
29	1.0	Ti alkoxid	0.5	1450°Cx5H	Ti-N-O	153	0.8
30	1.0	do.	1.0	do.	Ti-N-O	157	0.5
31	3.0	do.	0.5	do.	Ti-N-O	166	0.5
32	3.0	do.	1.0	do.	Ti-N-O	164	0.8
33	0.5	Ti stearate	0.3	1800°Cx3H	Ti-N-O	173	1.3
34	0.5	do.	0.6	do.	Ti-N-O	175	0.9
35	1.0	do.	0.3	do.	Ti-N-O	185	1.1
36	1.0	do.	0.6	do.	Ti-N-O	191	1.0
37	3.0	do.	0.3	do.	Ti-N-O	187	0.9
38	3.0	do.	0.6	do.	Ti-N-O	189	0.9
39	3.0	do.	0.3	1900°Cx5H	Ti-N-O	201	1.2
40	3.0	do.	0.0	do.	-----	194	10

Note: No. 40 is a comparative example wherein no Ti compound has been added.

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Example 6:

A CaCO_3 powder (average particle diameter: 1.5 μm) and a Y_2O_3 powder (average particle diameter: 0.5 μm) were added to an aluminum nitride powder having an average particle diameter of 0.87 μm (oxygen content: 0.9% by weight, carbon content: 0.03% by weight, content of impurities: 0.1% by weight or less). In this case, the CaCO_3 powder was added so that the mole ratio of the CaCO_3 in terms of CaO to the Y_2O_3 powder was 1 : 1. Titanium stearate, a TiO_2 powder (average particle diameter: 100 Å) and titanium alkoxide were added to the mixture. 5.0% by weight of an organic binder for molding was added to the mixture, and they were mixed with each other in a combined solvent comprising toluene and alcohol. The organic binder used for molding was a mixture of polyvinyl butyral (PVB) with dibutyl phthalate (DBP) in a ratio of 6 : 4. Thereafter, the mixture was dry-pressed to prepare a molding having a size of 25 x 25 x 1.0 (mm). The molding was heated in a nitrogen atmosphere at 600°C for 2 hr to remove the organic binder component. Thereafter, the treated molding was sintered in a nitrogen gas flow atmosphere having a CO gas concentration of 200 ppm or less under various conditions specified in Table 5.

The resultant sintered bodies were formed into sheets having a thickness of 0.5 ± 0.01 mm and subjected to measurements of the linear transmittance with FT-IR7000, manufactured by Japan Spectroscopic Co., Ltd., and the heat conductivity with a thermal constant measuring device TC-3000, manufactured by Shinkuu-Rikoh Inc. The results of the measurements are given in Table 5, from which it can be understood that the sintered bodies of the present invention are excellent in light shielding property and have a high



heat conductivity.

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Table 5:

No.	CaO+Y ₂ O ₃ amt. of addition, wt. %	Ti compd.	Amt. of addition wt. % (in terms of Ti)	Sintering conditions (°C x hr)	Ti compd. (according to ESCA)	Properties of sintered body	
						heat conductivity (W/m · K)	linear transmit- tance (%)
41	1.0	TiO ₂	0.01	1700°Cx3H	Ti-N-O	160	4.0
42	1.0	do.	0.05	do.	Ti-N-O	159	2.3
43	1.0	do.	0.10	do.	Ti-N-O	159	2.1
44	1.0	do.	0.50	do.	Ti-N-O	165	1.5
45	1.0	do.	1.0	do.	Ti-N-O	163	0.8
46	1.0	do.	5.0	do.	Ti-N-O	167	0.5
47	0.5	Ti alkoxide	0.5	1650°Cx5H	Ti-N-O	150	1.3
48	0.5	do.	1.0	do.	Ti-N-O	152	0.9
49	1.0	do.	0.5	do.	Ti-N-O	154	1.1
50	1.0	do.	1.0	do.	Ti-N-O	157	0.8
51	3.0	do.	0.5	do.	Ti-N-O	156	1.1

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Table 5: (contd.)

No.	CaO+Y ₂ O ₃ amt. of addition, wt. %	Ti compd.	Amt. of addition wt. % (in terms of Ti)	Sintering conditions (°C x hr)	Ti compd. (according to ESCA)	Properties of sintered body	
						heat conductivity (W/m · K)	linear transmit- tance (%)
52	3.0	Ti alkoxide	1.0	1650°Cx5H	Ti-N-O	154	1.0
53	0.5	Ti stearate	0.3	1800°Cx3H	Ti-N-O	185	1.3
54	0.5	do.	0.6	do.	Ti-N-O	180	1.1
55	1.0	do.	0.3	do.	Ti-N-O	193	1.0
56	1.0	Ti stearate	0.6	1800°Cx3H	Ti-N-O	191	0.7
57	3.0	do.	0.3	do.	Ti-N-O	199	1.1
58	3.0	do.	0.6	do.	Ti-N-O	198	0.8
59	3.0	do.	0.3	1700°Cx5H	Ti-N-O	179	1.1
60	3.0	-----	0.0	do.	-----	174	11

Note: No. 60 is a comparative example wherein no Ti compound has been added.

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Example 7:

A titanium compound in an amount of 0.2% by weight in terms of Ti and each sintering aid listed in Table 6 were added to an aluminum nitride powder
5 having an average particle diameter of 0.8 μ m (oxygen content: 1.5% by weight, carbon content: 0.03% by weight, content of metal impurities: 0.1% by weight or less). They were sufficiently mixed with each other in alcohol. The resultant mixture was dried and molded
10 on a single spindle press to prepare columnar moldings each having a diameter of 15 mm and a thickness of 1.5 mm. The thus-obtained moldings were heated in a hydrogen gas stream at 700°C for 30 min to remove the binder, and sintered in a nitrogen gas flow under
15 sintering conditions specified in Table 6. The properties of the resultant sintered bodies were measured in the same manner as that of the Example 6. The results of the measurements are given in the Table 6, from which it can be understood that the sintered
20 bodies of the present invention are excellent in light shielding property and have a high heat conductivity.

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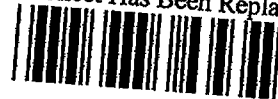


Table 6:

No.	Sintering aid	Amt. of addition, wt. %	Ti compd.	Sintering conditions ($^{\circ}\text{C} \times \text{hr}$)	Ti compd. (according to ESCA)	Properties of sintered body	
						heat conductivity ($\text{W/m} \cdot \text{K}$)	linear transmittance (%)
61	CaO	2.0	TiCO_3	$1800^{\circ}\text{C} \times 3\text{H}$	Ti-N-O	150	2.3
62	CaF_2	1.5	TiCO_3	do.	Ti-N-O	169	3.5
63	Gd_2O_3	1.5	TiCO_3	do.	Ti-N-O	159	2.1
64	$\text{Y}(\text{NO}_3)_3$	1.5	TiCO_3	do.	Ti-N-O	155	2.2
65	CaO Y_2O_3	0.39 1.5	TiCO_3	do.	Ti-N-O	158	2.0

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Industrial Applicability

As has been described hereinabove, according to the present invention, it is possible to provide an aluminum nitride sintered body excellent in light shielding property and heat conductivity and stabilized in these properties. The aluminum nitride sintered body of the present invention is used as a heat radiating substrate material or a heat radiating component for an IC substrate, IC package, etc., and can be applied to applications where the transmission of light is unfavorable, and components of an automation line wherein use is made of an optical sensor.

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Claims:

(1) An aluminum nitride sintered body characterized by comprising aluminum nitride as the main component, containing a titanium compound, and
5 having a black color, a transmittance of 10% or less with the light having a wavelength in the range of from 500 to 650 nm and a heat conductivity of 120 W/m·K or more.

(2) An aluminum nitride sintered body according to claim 1, wherein said titanium compound is Ti_nO_{2n-1} or a solid solution comprising Ti_nO_{2n-1} and nitrogen partly dissolved therein in the solid solution form
5 wherein n is 1 or more.

(3) An aluminum nitride sintered body according to claim 1, wherein said titanium compound is a compound represented by the formula TiN_xO_y wherein $0 < x < 1$ and y is $3/2 (1 - x)$.

(4) A process for producing an aluminum nitride sintered body, characterized by adding 0.05 to 5% by weight, in terms of Ti, of a titanium compound and a sintering aid to an aluminum nitride powder, molding
5 the mixture, heating the molding in vacuo, air, a nitrogen gas, a hydrogen gas or an atmosphere comprising a mixture of these gases until the residual carbon content is reduced to 0.2% by weight or less, and sintering the mixture in a nonoxidizing atmosphere
10 containing nitrogen at 1600°C or above.

(5) A process for producing an aluminum nitride sintered body according to claim 4, wherein said sintering aid compound comprises at least one compound selected among those of rare earth elements and
5 alkaline earth elements.

(6) A process for producing an aluminum nitride



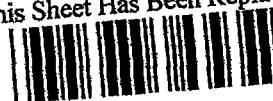


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sintered body, characterized by adding 0.05 to 5% by weight, in terms of Ti, of a titanium compound, a compound capable of forming carbon after being
5 thermally decomposed and a sintering aid to an aluminum nitride powder, molding the mixture, heating the molding in vacuo, air or a nitrogen gas, a hydrogen gas or an atmosphere comprising a mixture of these gases until the residual carbon content is
10 reduced to 0.2 to 2.0% by weight, and sintering the mixture in a nonoxidizing atmosphere containing nitrogen at 1600°C or above.

(7) A process for producing an aluminum nitride sintered body according to claim 6, wherein said sintering aid compound comprises at least one compound selected among those of rare earth elements and
5 alkaline earth elements.

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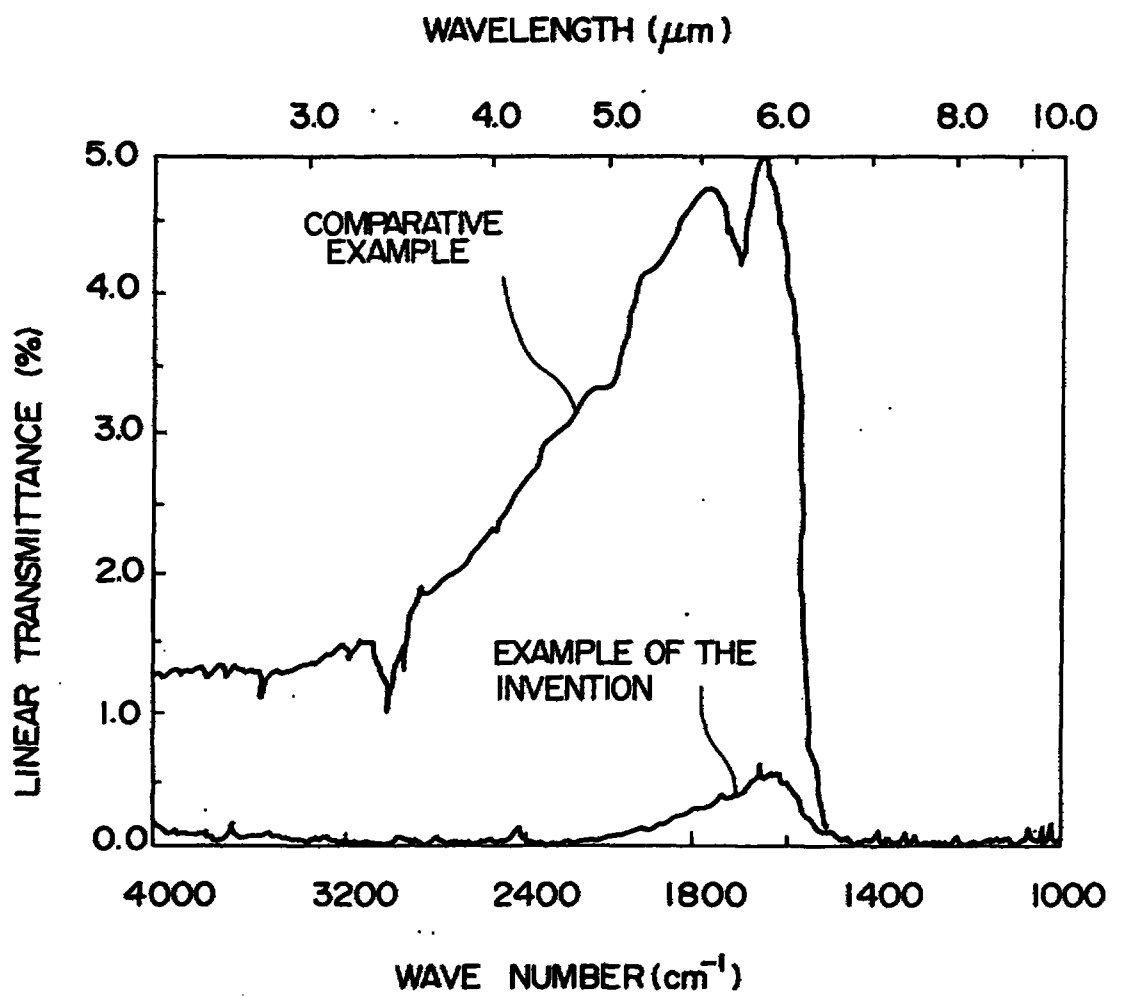
ABSTRACT

An aluminum nitride sintered body characterized by comprising aluminum nitride as the main component, containing a titanium compound, and having a black color, a transmittance of 10% or less with the light
5 having a wavelength in the range of from 500 to 650 nm and a heat conductivity of 120 W/m·K or more. The sintered body is produced by adding 0.05 to 5% by weight, in terms of Ti, of a titanium compound and a sintering aid compound and, if necessary, a compound
10 capable of forming carbon after being thermally decomposed to an aluminum nitride powder, molding the mixture, heating the molding in vacuo, air or a nitrogen gas, a hydrogen gas or an atmosphere comprising a mixture of these gases until the residual
15 carbon content is reduced to 2.0% by weight or less, and sintering the heat-treated mixture in a nonoxidizing atmosphere containing nitrogen at 1600°C or above. The titanium compound is Ti_nO_{2n-1} or a solid solution comprising Ti_nO_{2n-1} and nitrogen partly dissolved therein in the solid solution form wherein n
20 is 1 or more, or a compound represented by the formula TiN_xO_y wherein $0 < x < 1$ and y is $3/2 (1 - x)$.

There is provided an aluminum nitride sintered body wherein both the light shielding property and the
25 heat conductivity are stabilized.



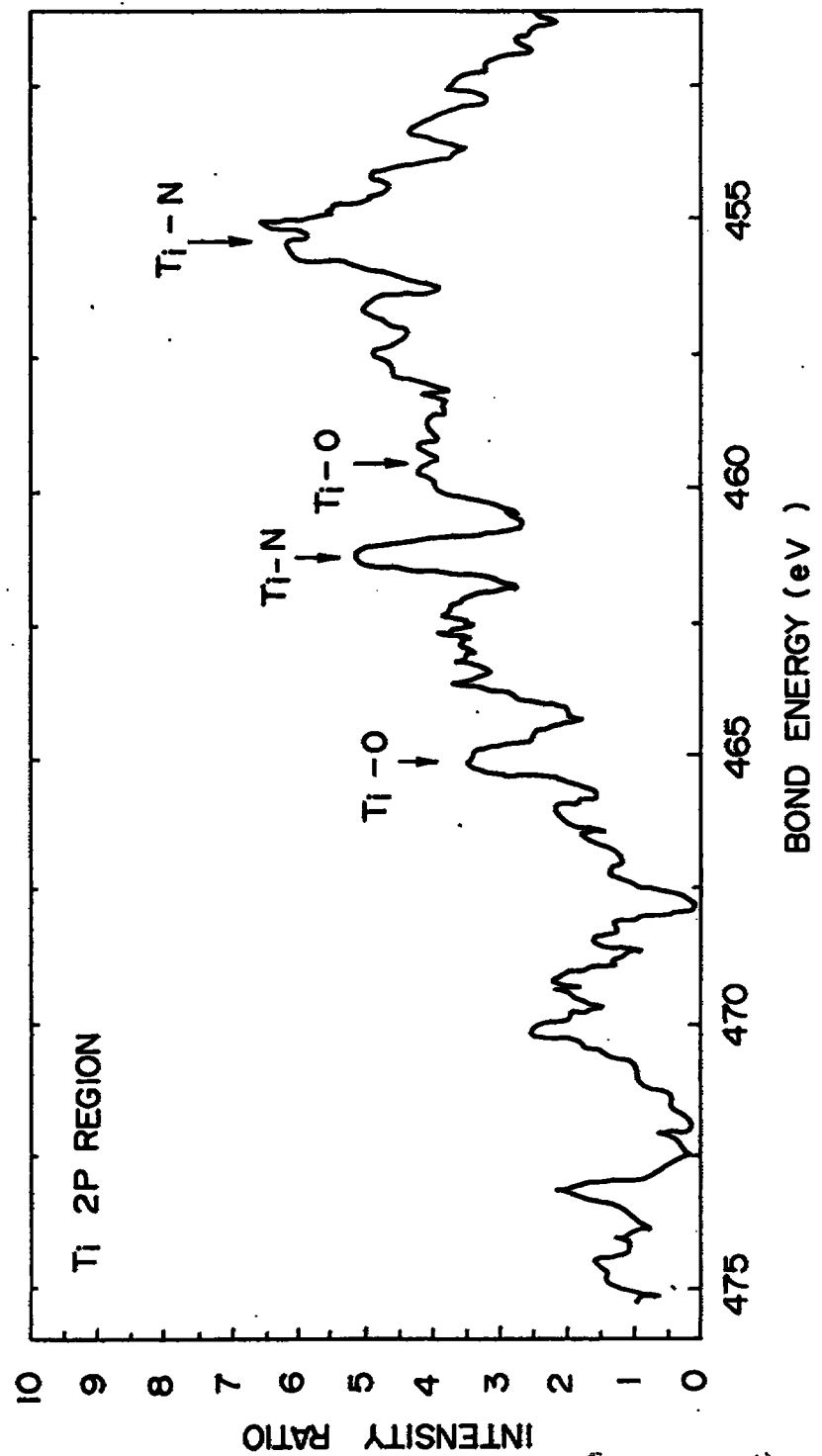
FIG. 1



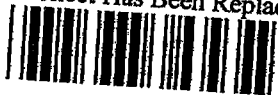
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FIG. 2



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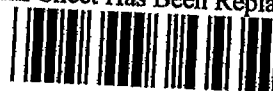
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ABSTRACT

ALUMINUM NITRIDE SINTERED BODY AND PROCESS FOR PRODUCING THE SAME

A sinter which is based on aluminum nitride, contains a titanium compound, is black, and has a transmittance of 10% or less as regards the light with a wavelength of 500 to 650 nm and a thermal conductivity of 120 W/m°K or above. It is produced by molding a mixture of aluminum nitride powder with a titanium compound in an amount of 0.05 to 5 wt% in terms of titanium element, a sintering aid and optionally further a compound which generates carbon by thermal decomposition, heating the molded article in a vacuum, air, nitrogen, hydrogen or a mixture thereof to a residual carbon content of 2.0 wt% or less, and sintering in a nitrogen-containing nonoxidative atmosphere at 1,600°C or above. Examples of the titanium compound to be used include Ti_nO_{2n-1} solid solution comprising Ti_nO_{2n-1} and nitrogen partially dissolved therein, wherein n is 1 or above, and TiN_xO_y wherein $0 < x < 1$ and $y = 3/2 (1-x)$. The obtained sinter has stable light shielding property and thermal conductivity.

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☒ Claim(s)	: paged 1... to paged 3	
☒ Drawing(s)	: paged 1/2 to paged 3/2	
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DESCRIPTION

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ALUMINUM NITRIDE SINTERED BODY AND
PROCESS FOR PRODUCING THE SAME

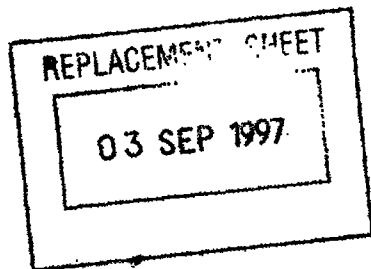
TECHNICAL FIELD

The present invention relates to an aluminum
5 nitride sintered body and a process for producing the
same, in particular to an aluminum nitride sintered
body which is black and has a high heat conductivity.

BACKGROUND ART

In recent years, the technical advance of a
10 large scale integrated circuit (LSI) device is
significant and, in particular, an improvement in the
integration density is remarkable. With an
improvement in the integration density, the size of
the IC chip has been increased and the density of the
15 wiring per IC chip has been increased. This has led
to a remarkable increase in the heat build up per IC
chip. For this reason, great importance has come to
be placed on the heat radiating property of a material
constituting a package on which IC chips are mounted.
20 An alumina sintered body has hitherto found extensive
use as the material of an IC chip substrate. With the
heat conductivity of the alumina sintered body,
however, it is becoming difficult to ensure a heat
radiating property sufficient to cope with an increase
25 in the heat buildup of the IC chip. Studies have been
made also on the use of a beryllium oxide sintered
body having a high heat conductivity as an alternative
to the alumina sintered body. The beryllium oxide is,

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however, difficult to handle due to the toxicity of the material per se and therefore can be used for a special application only.

On the other hand, an aluminum nitride sintered
5 body has a heat conductivity (theoretical value: 320 W/m·K) comparable with that of the beryllium oxide sintered body, is nontoxic and has a high insulating property. Therefore, it has attracted special interest recently in the field of semiconductor industries and
10 electronics including a high output laser, wherein the heat radiating property becomes an issue.

As described above, aluminum nitride is theoretically a material having a high heat conductivity and a high insulating property as a
15 single crystal. Since, however, aluminum nitride is a material having a covalent bond character of 50%, the diffusion coefficient of the constituent elements is small. Further, the sinterability of the aluminum nitride powder is much lower than that of the aluminum
20 oxide powder. Therefore, when a sintered body is produced from the aluminum nitride powder, the relative density (based on the theoretical density of aluminum nitride, that is, 3.26 g/cm^3) of the aluminum nitride sintered body produced by powder molding
25 followed by sintering is as low as 70 to 80% although it depends upon the sintering conditions, and the sintered body has a large amount of pores.

On the other hand, the heat conduction of the aluminum nitride sintered body having an insulating
30 property occurs through the movement of phonons as pseudo-particles. For this reason, defects such as pores or impurities in the crystal lattice cause scattering of phonons, which brings about a lowering in the heat conductivity of the aluminum nitride

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sintered body.

Under these circumstances, various proposals have been made for the purpose of producing an aluminum nitride sintered body having a high conductivity.

In order to produce an aluminum nitride sintered body having a high conductivity, however, it is necessary to use a starting material having a high purity and to prevent the contamination with impurities in the manufacturing process. The resultant aluminum nitride sintered body is limited to a white or thinly colored sintered body, which renders the sintered body unusable in applications where the transmission of light becomes a problem. For this reason, the development of a colored aluminum nitride sintered body has been desired in such applications.

The present inventors have already proposed a highly heat conductive aluminum nitride sintered body having a light shielding property in Japanese Patent Laid-Open No. 124772/1990.

In the conventional light shielding aluminum nitride sintered body, the light shielding property is obtained by distributing a transition metal compound in the sintered body and allowing the light to be absorbed or diffused in the compound. No properties of the aluminum nitride sintered body, such as heat conductivity, can be sufficiently obtained depending upon the type of the transition metal added. This appears to derive from the fact that the transition metal compound in the aluminum nitride sintered body is not sufficiently controlled.

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Accordingly, an object of the present invention is to eliminate the above-described problem and, at the same time , to provide an aluminum nitride sintered body stabilized in the properties such as light shielding property and heat conductivity and a process for producing the same.

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DISCLOSURE OF THE INVENTION

The present inventors have made detailed studies on an aluminium nitride sintered body and, as a result, have found that particularly the addition of a
5 titanium compound as a means for stabilizing the heat conductivity and meeting the light shielding property requirements serves to stabilize both the light shielding property and the heat conductivity.

Accordingly, the present invention relates to an
10 aluminium nitride sintered body characterized by the features of claim 1.

The titanium compound includes Ti_nO_{2n-1} or a solid solution comprising Ti_nO_{2n-1} and nitrogen partly dissolved therein in the solid solution form wherein n
15 is 1 or more. The n value may vary widely. When n is 1, the titanium compound is TiO and, for example, when n is 10, it is $Ti_{10}O_{19}$. The object of the present invention can be attained so far as the titanium compound is none of TiN and TiO_2 . It is
20 conceivable that the Ti_nO_{2n-1} may contain nitrogen in a solid solution form. However, it is difficult to determine the amount of such nitrogen by analysis.

The content of Ti_nO_{2n-1} in aluminium nitride is 0.01 to 5.0% by weight, preferably 0.05 to 1.0% by
25 weight, in terms of Ti. When the content is less than

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0.01% by weight, the light shielding property is unsatisfactory. On the other hand, when it exceeds 5.0% by weight, the insulating property deteriorates.

Further, the titanium compound includes a compound represented by the formula TiN_xO_y wherein $0 < x < 1$ and y is $3/2 \cdot (1 - x)$. It is possible that the y value varies widely. When the x value is 0.95, the compound is $TiN_{0.95}O_{0.075}$. The X-ray diffractometry of TiN_xO_y comprising TiN and oxygen dissolved therein in the form of a solid solution reveals that the titanium compound has a TiN crystalline structure. The amount of oxygen in the solid solution form is determined by estimating the bond energy of elementary titanium according to ESCA (X-ray photoelectron spectroscopy) to simultaneously determine two kinds of bonding states, that is, the energy of bonding between a titanium atom and an oxygen atom of 459 and 465 eV (± 1 eV) and the energy of bonding between a titanium atom and a nitrogen atom of 456 and 462 eV (± 1 eV).

The content of the Ti-N-O compound in the aluminum nitride powder or aluminum nitride sintered body is 0.01 to 5.0% by weight in terms of Ti. When the content is less than 0.01% by weight, the shielding property of the aluminum nitride sintered body is unsatisfactory, while when it exceeds 5.0% by weight, the insulating property of the aluminum nitride sintered body deteriorates.

According to a preferred embodiment of the aluminum nitride sintered body of the present invention, the sintered body has a linear transmittance of 5% or less with the light having a wavelength of 500 nm or a linear transmittance of 10% or less with the light having a wavelength of 6.0 μm and a heat conductivity of 120 W/m·K or more in terms

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of a sample thickness of 0.5 mm.

The present invention also provides a process for producing an aluminum nitride sintered body characterized by adding 0.01 to 5% by weight, in terms of Ti, of a titanium compound and a sintering aid to an aluminum nitride powder, molding the mixture, heating the molding in vacuo, air, a nitrogen gas, a hydrogen gas or an atmosphere comprising a mixture of these gases until the residual carbon content is reduced to 0.2% by weight or less, and sintering the heat-treated mixture in a nonoxidizing atmosphere containing nitrogen at 1600°C or above.

Further, the present invention provides a process for producing an aluminum nitride sintered body characterized by adding 0.01 to 5% by weight, in terms of Ti element, of a titanium compound, a compound capable of forming carbon after being thermally decomposed and a sintering aid to an aluminum nitride powder, molding the mixture, heating the molding in vacuo, air, a nitrogen gas, a hydrogen gas or an atmosphere comprising a mixture of these gases until the residual carbon content is reduced to 0.2 to 2.0% by weight, and sintering the heat-treated mixture in a nonoxidizing atmosphere containing nitrogen at 1600°C or above.

In the process according to the present invention, it is preferred to use an aluminum nitride powder having a high purity. For example, it is preferred that the absorption peak of aluminum nitride (wherein aluminum is coordinated with four nitrogen atoms) obtained by an infrared absorption method using KBr be observed at 750 cm^{-1} or less. In particular, in the aluminum nitride powder, the amount of oxygen, carbon, etc., in the solid solution form in the

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aluminum nitride powder particle and the amount of metallic elements as impurities included in the powder should be small.

5 The titanium compound to be added to the aluminum nitride powder should be convertible into metallic titanium, TiO or TiO_2 when heated. Preferred examples of such a compound include organometallic compounds, metal alkoxide compounds and stearates. The amount of addition of the titanium compound is
10 still preferably in the range of from 0.05 to 5.0% by weight in terms of Ti for the reasons as described above. The titanium compound to be added may also be TiO_2 (having a rutile crystal structure) comprising ultrafine particles having a primary particle diameter
15 of 500 nm or less.

At least one compound selected among those of rare earth elements and alkaline earth elements is used as the sintering aid. The amount of addition of the sintering aid is preferably in the range of from
20 0.01 to 10.0% by weight in terms of oxide. The addition of the sintering aid facilitates the production of an aluminum nitride sintered body having a high density, so that the object of the present invention can be attained.

25 The above-described starting materials are mixed together and molded, and the resultant molding is heated at 200 to 1000°C in the air, vacuo, a nitrogen gas, a hydrogen gas or an atmosphere comprising a mixture of these gases. The content of the residual
30 carbon is regulated by either adding a compound capable of forming carbon after being thermally decomposed or not. In this case, the reason why the heating atmosphere is limited as described above resides in that the aluminum nitride powder suffers no

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significant oxidation and the residual carbon content can be regulated thereby. The term "residual carbon" used herein is intended to mean liberated carbon. The residual carbon content is limited to 2.0% by weight or less because when the content exceeds 2.0% by weight, TiN and TiC are formed and besides the relative density of the aluminum nitride sintered body is reduced to 90% or less.

The molding thus treated is sintered at a temperature of 1600°C or above in a nonoxidizing atmosphere containing nitrogen.

BRIEF DESCRIPTION OF DRAWINGS

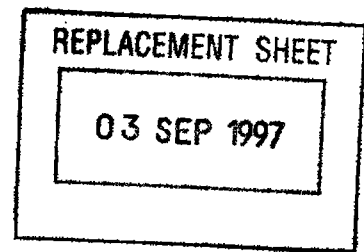
FIG. 1 is a graph showing the results of measurement of the linear transmittance for a wavelength area near 6μm of an aluminium nitride sintered body prepared in Example 3, and FIG. 2 is a graph showing the results of the ESCA analysis of an aluminium nitride sintered body prepared in Example 3.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will now be described in more detail with reference to the following Examples.

Example 1:

An Y_2O_3 powder (particle diameter: 0.5 μm) and a titanium compound of the type and in an amount as specified in Table 1 were added to an AlN powder having an average particle diameter of 0.8 μm (oxygen: 1.5%, carbon: 0.03%, metal impurities: 0.1% or less in total). They were mixed with each other in alcohol, dried and molded on a dry press to prepare moldings each having a diameter of 15 mm and a thickness of 3



mm. The moldings were heated in the air at 400°C for 30 min to remove the binder, and sintered in a nitrogen gas flow under sintering conditions specified in the Table 1. The properties of the resultant sintered bodies are also given therein. As is apparent from the table, according to the present invention, it is possible to produce an AlN sintered body having an excellent shielding property and a high heat conductivity.

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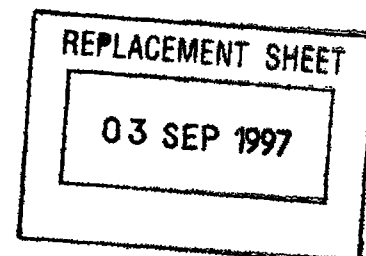
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Table 1:

No.	Y ₂ O ₃ amt. of addition	Ti compd.	Amount of addition wt. % (in terms of Ti)	Sintering conditions (°C x H)	Ti compd. (according to TEM)	Properties of sintered body	
						heat conductivity (W/m·K)	transmittance (%)
*1	3.0%	Ti alkoxide	0.01	1850°Cx3H	TiO	180	15
2	do.	do.	0.07	do.	TiO	170	4
3	do.	do.	0.20	do.	TiO	170	2
4	do.	do.	0.70	do.	TiO	170	1
5	do.	do.	2.0	do.	TiO	160	1
6	do.	Ti stearate	0.5	do.	TiO	170	1
7	1.0	do.	do.	do.	TiO	170	1
8	0.5	do.	do.	do.	TiO	170	1
9	7.0	do.	do.	do.	TiO	170	1
10	1.0	do.	do.	1750°Cx3H	TiO	180	1
					TiO	170	1

Note: * Comparative Example



Example 2:

5 A titanium compound in an amount of 0.2% by weight in terms of Ti and a sintering aid listed in Table 2 were added to an AlN powder having an average
10 particle diameter of 0.8 μ m (oxygen: 1.5%, carbon: 0.03%, metal impurities: 0.1% or less in total). They were sufficiently mixed with each other in alcohol, dried and molded on a simple spindle press to prepare moldings each having a diameter of 15 mm and a
15 thickness of 3 mm. The moldings were heated in a steam stream at 700°C for 30 min to remove the binder, and sintered in a nitrogen gas flow under sintering conditions specified in the Table 2. The properties of the resultant sintered bodies are also given therein.

As is apparent from the table, according to the present invention, it is possible to produce an AlN sintered body having an excellent shielding property and a high heat conductivity.

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Table 2:

No.	Sintering aid	Amt. of addition wt%	Ti compd.	Sintering conditions ($^{\circ}\text{C} \times \text{H}$)	Ti compd.	Properties of sintered body	
						heat conductivity ($\text{W/m}\cdot\text{K}$)	transmittance (%)
11	CaO	2.0	TiCO_3	$1800^{\circ}\text{C} \times 3\text{H}$	TiO	130	1
12	CaO	0.8	TiCO_3	do.	TiO	130	1
13	CaO Y_2O_3	0.8 1.5	TiO_2	do.	TiO	150	1
14	Gd_2O_3	1.5	TiO_2	do.	TiO	130	1
15	$\text{Y}(\text{NO}_3)_3$	1.5	TiO_2	do.	TiO	140	1

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Example 3:

5 A Y_2O_3 powder (particle diameter: 0.5 μm) and titanium stearate in an amount of 0.3% by weight in terms of titanium were added to an aluminum nitride
10 powder having an average particle diameter of 1.5 μm (oxygen content: 1.5% by weight, carbon content: 0.04% by weight, content of metal impurities: 0.1% by weight or less). 11% by weight of an organic binder for molding was added to the mixed powder, and they were
15 mixed with each other in a combined solvent comprising toluene and alcohol. The organic binder used was a mixture of polyvinyl butyral (PVB) with dibutyl phthalate (DBP) in a ratio of 6 : 4. Thereafter, the mixture was molded by the doctor blade method into a sheet having a thickness of 0.8 mm. The molding was heated in a nitrogen atmosphere at 600°C for 2 hr to remove the organic binder component. Thereafter, the molding was sintered in a nitrogen gas atmosphere having a CO gas concentration of 200 ppm or less at
20 1850°C for 1 hr.

The resultant aluminum nitride sintered body was molded into a sheet having a thickness of 0.5 ± 0.01 mm and subjected to measurement of the linear transmittance with FT-IR7000, manufactured by Japan Spectroscopic Co., Ltd., and the heat conductivity with a thermal constant measuring device TC-3000, manufactured by Shinkuu-Rikoh Inc.

30 A sintered body wherein no titanium stearate had been added was prepared as a comparative sample under the same condition as that described above. The results of the measurement of the linear transmittance for a wavelength area near 6 μm are shown in FIG. 1. The heat conductivity of the sintered body according to the example of the present invention was 185 W/m.K, while that of the aluminum

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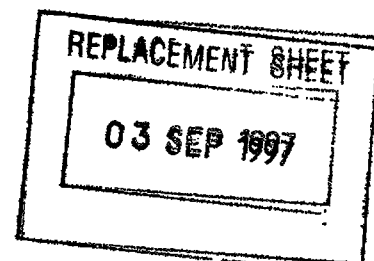
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nitride sintered body according to the comparative example was 183 W/m·K. As is apparent from the results, the aluminum nitride sintered body of the present invention is excellent in light shielding property and has a high heat conductivity.

FIG. 2 shows the results of the ESCA analysis of a sintered body wherein titanium stearate has been added. The figure shows the presence of bond energy levels of 456 eV, 459 eV, 462 eV and 465 eV. The bond energies of 459 eV and 465 eV refer to a bond between the titanium atom and the oxygen atom, while those of 456 and 462 eV refer to a bond between the titanium atom and the nitrogen atom.

Example 4:

A Y_2O_3 powder (average particle diameter: 0.5 μm), titanium stearate, a TiO_2 powder (average particle diameter: 100 Å) and a titanium alkoxide were added to an aluminum nitride powder having an average particle diameter of 1.5 μm (oxygen content: 1.5% by weight, carbon content: 0.04% by weight, content of metal impurities: 0.1% by weight or less). 11% by weight of an organic binder for molding was added to the mixed powder, and they were mixed with each other in a combined solvent comprising toluene and alcohol. The organic binder for molding used was a mixture of polyvinyl butyral (PVB) with dibutyl phthalate (DBP) in a ratio of 6 : 4. Thereafter, the mixture was molded by the doctor blade method into a sheet having a thickness of 0.8 mm. The molding was heated in a nitrogen atmosphere at 600 °C for 2 hr to remove the organic binder component. Thereafter, the molding thus obtained was sintered in a nitrogen gas flow atmosphere having a CO gas concentration of 200 ppm or less under various conditions specified in Table 3.



The resultant aluminum nitride sintered bodies were molded into sheets each having a thickness of 0.5 ± 0.01 mm and subjected to measurements of the linear transmittance with FT-IR7000, manufactured by Japan Spectroscopic Co., Ltd., and the heat conductivity with a thermal constant measuring device TC-3000, manufactured by Shinkuu-Rikoh Inc.

The results of the measurements are given in the Table 3, from which it can be understood that the sintered bodies of the present invention are excellent in light shielding property and have a high heat conductivity.

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Table 3:

No.	Y ₂ O ₃ amt. of addition wt. %	Ti compd.	Amt. of addition, wt. % (in terms of Ti)	Sintering conditions (°C x hr)	Ti compd. (according to ESCA)	Properties of sintered body	
						heat conductivity (W/m·K)	transmit- tance (%)
1	1.0	TiO ₂	0.01	1850°Cx2H	Ti-N-O	180	3.0
2	1.0	do.	0.05	do.	Ti-N-O	182	2.3
3	1.0	do.	0.10	do.	Ti-N-O	180	1.5
4	1.0	do.	0.50	do.	Ti-N-O	178	1.0
5	1.0	do.	1.0	do.	Ti-N-O	175	0.5
6	1.0	do.	5.0	do.	Ti-N-O	170	0.5
7	0.5	Ti alkoxide	0.5	1750 °Cx5H	Ti-N-O	150	1.0
8	0.5	do.	1.0	do.	Ti-N-O	155	0.6
9	1.0	do.	0.5	do.	Ti-N-O	158	0.9
10	1.0	do.	1.0	do.	Ti-N-O	157	0.7
11	5.0	do.	0.5	do.	Ti-N-O	166	1.0

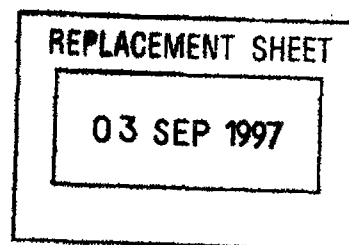
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Table 3: (contd.)

No.	Y ₂ O ₃ amt. of addition wt. %	Ti compd.	Amt. of addition wt. % (in terms of Ti)	Sintering conditions (°C x H)	Ti compd. (according to ESCA)	Properties of sintered body	
						heat conductivity (W/mK)	transmittance (%)
12	5.0	Ti alkoxide	1.0	1750°C x 5H	Ti-N-O	164	1.1
13	0.5	Ti stearate	0.3	1800°C x 3H	Ti-N-O	193	1.2
14	0.5	do.	0.6	do.	Ti-N-O	195	0.8
15	1.0	do.	0.3	do.	Ti-N-O	225	1.4
16	1.0	Ti stearate	0.6	1800°C x 3H	Ti-N-O	201	0.7
17	3.0	do.	0.3	do.	Ti-N-O	197	1.1
18	3.0	Ti stearate	0.6	do.	Ti-N-O	189	0.6
19	5.0	do.	0.3	do.	Ti-N-O	210	1.0
20	5.0	-----	0.0	do.	-----	194	11

Note: No. 20 is a comparative example wherein no Ti compound has been added.



Example 5 :

A CaO powder (average particle diameter : 1.5 μm) and titanium stearate, TiO_2 or titanium alkoxide were added to an aluminum nitride powder having an average particle diameter of 1.5 μm (oxygen content: 1.4% by weight, content of impurities: 0.1 % by weight or less). The organic binder for molding used was a mixture of polyvinyl butyral (PVB) with dibutyl phthalate (DBP) in a ratio of 6 : 4. Thereafter, the mixture was molded by the doctor blade method into a sheet having a thickness of 0.8 mm. The molding was heated in a nitrogen atmosphere at 600°C for 2 hr to remove the organic binder component. Thereafter, the molding was sintered in a nitrogen gas flow atmosphere having a CO gas concentration of 200 ppm or less under various conditions specified in Table 4.

The resultant aluminum nitride sintered bodies were molded into sheets each having a thickness of 0.5 $\pm$ 0.01 mm and subjected to measurements of the linear transmittance with FT-IR7000, manufactured by Japan Spectroscopic Co., Ltd., and the heat conductivity with a thermal constant measuring device TC-3000, manufactured by Shinkuu-Rikoh Inc.

The results of the measurements are given in the Table 4, from which it can be understood that the sintered bodies of the present invention are excellent in light shielding property and having a high heat conductivity.

Table 4:

No.	CaO amt. of addition, wt. %	Ti compd.	Amt. of addition wt. % (in terms of Ti)	Sintering conditions (° C x H)	Ti compd. (according to ESCA)	Properties of sintered body	
						heat conductivity (W/m · K)	linear transmit- tance (%)
21	1.0	TiO ₂	0.01	1750°Cx3H	Ti-N-O	162	3.8
22	1.0	do.	0.05	do.	Ti-N-O	163	2.3
23	1.0	do.	0.10	do.	Ti-N-O	169	2.1
24	1.0	do.	0.50	do.	Ti-N-O	167	1.0
25	1.0	do.	1.0	do.	Ti-N-O	166	0.8
26	1.0	do.	5.0	do.	Ti-N-O	170	0.7
27	0.5	Ti alkoxide	0.5	1450°Cx5H	Ti-N-O	150	0.9
28	0.5	do.	1.0	do.	Ti-N-O	145	0.7

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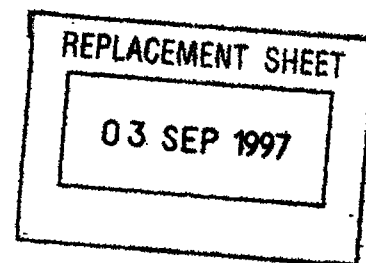
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Table 4: (contd.)

No.	CaO amt. of addition, wt. %	Ti compd.	Amt. of addition - wt. % (in terms of Ti)	Sintering conditions (°C x H)	Ti compd. (according to ESCA)	Properties of sintered body	
						heat conductivity (W/m · K)	linear transmit- tance (%)
29	1.0	Ti alkoxid	0.5	1450°Cx5H	Ti-N-O	153	0.8
30	1.0	do.	1.0	do.	Ti-N-O	157	0.5
31	3.0	do.	0.5	do.	Ti-N-O	166	0.5
32	3.0	do.	1.0	do.	Ti-N-O	164	0.8
33 *	0.5	Ti stearate	0.3	1800°Cx3H	Ti-N-O	173	1.3
34	0.5	do.	0.6	do.	Ti-N-O	175	0.9
35	1.0	do.	0.3	do.	Ti-N-O	185	1.1
36	1.0	do.	0.6	do.	Ti-N-O	191	1.0
37	3.0	do.	0.3	do.	Ti-N-O	187	0.9
38	3.0	do.	0.6	do.	Ti-N-O	189	0.9
39	3.0	do.	0.3	1900°Cx5H	Ti-N-O	201	1.2
40	3.0	do.	0.0	do.	-----	194	10

Note: No. 40 is a comparative example wherein no Ti compound has been added.



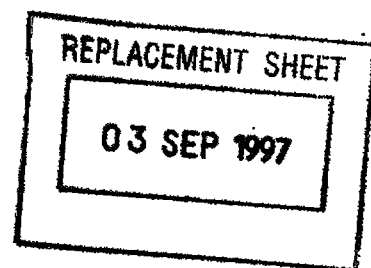
Example 6:

A CaCO_3 powder (average particle diameter: 1.5 μm) and a Y_2O_3 powder (average particle diameter: 0.5 μm) were added to an aluminum nitride powder having an average particle diameter of 0.87 μm (oxygen content: 0.9% by weight, carbon content: 0.03% by weight, content of impurities: 0.1% by weight or less). In this case, the CaCO_3 powder was added so that the mole ratio of the CaCO_3 in terms of CaO to the Y_2O_3 powder was 1 : 1. Titanium stearate, a TiO_2 powder (average particle diameter: 100 Å) and titanium alkoxide were added to the mixture. 5.0% by weight of an organic binder for molding was added to the mixture, and they were mixed with each other in a combined solvent comprising toluene and alcohol. The organic binder used for molding was a mixture of polyvinyl butyral (PVB) with dibutyl phthalate (DBP) in a ratio of 6 : 4. Thereafter, the mixture was dry-pressed to prepare a molding having a size of 25 x 25 x 1.0 (mm). The molding was heated in a nitrogen atmosphere at 600°C for 2 hr to remove the organic binder component. Thereafter, the treated molding was sintered in a nitrogen gas flow atmosphere having a CO gas concentration of 200 ppm or less under various conditions specified in Table 5.

The resultant sintered bodies were formed into sheets having a thickness of 0.5 ± 0.01 mm and subjected to measurements of the linear transmittance with FT-IR7000, manufactured by Japan Spectroscopic Co., Ltd., and the heat conductivity with a thermal constant measuring device TC-3000, manufactured by Shinkuu-Rikoh Inc. The results of the measurements are given in Table 5, from which it can be understood that the sintered bodies of the present invention are excellent in light shielding property and have a high

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heat conductivity.



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Table 5:

No.	CaO+Y ₂ O ₃ amt. of addition, wt. %	Ti compd.	Amt. of addition wt. % (in terms of Ti)	Sintering conditions (°C x hr)	Ti compd. (according to ESCA)	Properties of sintered body	
						heat conductivity (W/m · K)	linear transmit- tance (%)
41	1.0	TiO ₂	0.01	1700°Cx3H	Ti-N-O	160	4.0
42	1.0	do.	0.05	do.	Ti-N-O	159	2.3
43	1.0	do.	0.10	do.	Ti-N-O	159	2.1
44	1.0	do.	0.50	do.	Ti-N-O	163	1.5
45	1.0	do.	1.0	do.	Ti-N-O	163	0.8
46	1.0	do.	5.0	do.	Ti-N-O	167	0.5
47	0.5	Ti alkoxide	0.5	1650°Cx5H	Ti-N-O	150	1.3
48	0.5	do.	1.0	do.	Ti-N-O	152	0.9
49	1.0	do.	0.5	do.	Ti-N-O	154	1.1
50	1.0	do.	1.0	do.	Ti-N-O	157	0.8
51	3.0	do.	0.5	do.	Ti-N-O	156	1.1

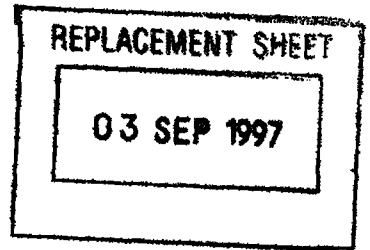
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Table 5: (contd.)

No.	CaO+Y ₂ O ₃ amt. of addition, wt. %	Ti compd.	Amt. of addition wt. % (in terms of Ti)	Sintering conditions (°C x hr)	Ti compd. (according to ESCA)	Properties of sintered body	
						heat conductivity (W/m · K)	linear transmit- tance (%)
52	3.0	Ti alkoxide	1.0	1650°Cx5H	Ti-N-O	154	1.0
53	0.5	Ti stearate	0.3	1800°Cx3H	Ti-N-O	185	1.3
54	0.5	do.	0.6	do.	Ti-N-O	180	1.1
55	1.0	do.	0.3	do.	Ti-N-O	193	1.0
56	1.0	Ti stearate	0.6	1800°Cx3H	Ti-N-O	191	0.7
57	3.0	do.	0.3	do.	Ti-N-O	199	1.1
58	3.0	do.	0.6	do.	Ti-N-O	198	0.8
59	3.0	do.	0.3	1700°Cx5H	Ti-N-O	179	1.1
60	3.0	-----	0.0	do.	-----	174	11

Note: No. 60 is a comparative example wherein no Ti compound has been added.



Example 7:

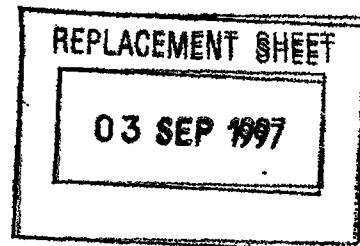
A titanium compound in an amount of 0.2% by weight in terms of Ti and each sintering aid listed in Table 6 were added to an aluminum nitride powder having an average particle diameter of 0.8 μm (oxygen content: 1.5% by weight, carbon content: 0.03% by weight, content of metal impurities: 0.1% by weight or less). They were sufficiently mixed with each other in alcohol. The resultant mixture was dried and molded on a single spindle press to prepare columnar moldings each having a diameter of 15 mm and a thickness of 1.5 mm. The thus-obtained moldings were heated in a hydrogen gas stream at 700°C for 30 min to remove the binder, and sintered in a nitrogen gas flow under sintering conditions specified in Table 6. The properties of the resultant sintered bodies were measured in the same manner as that of the Example 6. The results of the measurements are given in the Table 6, from which it can be understood that the sintered bodies of the present invention are excellent in light shielding property and have a high heat conductivity.

Table 6:

No.	Sintering aid	Amt. of addition, wt. %	Ti compd.	Sintering conditions (°C x hr)	Ti compd. (according to ESCA)	Properties of sintered body	
						heat conductivity (W/m · K)	linear transmittance (%)
61	CaO	2.0	TiCO ₃	1800°Cx3H	Ti-N-O	150	2.3
62	CaF ₂	1.5	TiCO ₃	do.	Ti-N-O	169	3.5
63	Gd ₂ O ₃	1.5	TiCO ₃	do.	Ti-N-O	159	2.1
64	Y(NO ₃) ₃	1.5	TiCO ₃	do.	Ti-N-O	155	2.2
65	CaO Y ₂ O ₃	0.39 1.5	TiCO ₃	do.	Ti-N-O	158	2.0

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Industrial Applicability

As has been described hereinabove, according to the present invention, it is possible to provide an aluminum nitride sintered body excellent in light shielding property and heat conductivity and stabilized in these properties. The aluminum nitride sintered body of the present invention is used as a heat radiating substrate material or a heat radiating component for an IC substrate, IC package, etc., and can be applied to applications where the transmission of light is unfavorable, and components of an automation line wherein use is made of an optical sensor.



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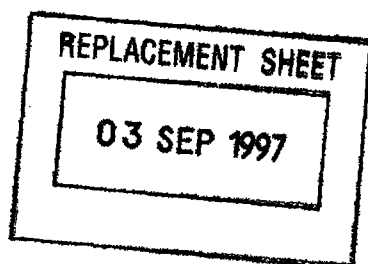
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Claims :

(1) An aluminum nitride sintered body comprising aluminum nitride as the main component, and a titanium compound selected from the group consisting of Ti_nO_{2n-1} , a solid solution comprising Ti_nO_{2n-1} and nitrogen partly dissolved therein in solid solution form, and TiN_xO_y wherein $0 < x < 1$, y is $3/2(1-x)$, and n is at least 1, said sintered body having a black color, a linear transmittance of not more than 10% for light having a wavelength of 500 to 650nm and a heat conductivity of 120 W/m.K or more.

(2) A process for producing an aluminum nitride sintered body according to claim 1, characterized by adding 0.01 to 5% by weight, in terms of Ti, of a titanium compound and a sintering aid to an aluminum nitride powder, molding the mixture, heating the molding in vacuo, air, a nitrogen gas, a hydrogen gas or an atmosphere comprising a mixture of these gases until the residual carbon content is reduced to 0.2% by weight or less, and sintering the mixture in a nonoxidizing atmosphere containing nitrogen at 1600°C or above.

(3) A process according to claim 2, wherein said sintering aid compound comprise at least one compound selected among those of rare earth elements and alkaline earth elements.



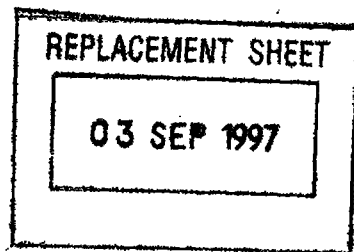
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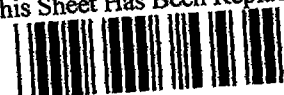
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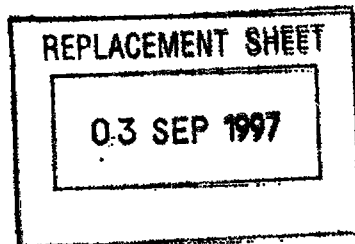
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(4) The sintered body according to claim 1, wherein
the sintered body has a linear transmittance of 5% or
less with the light having a wavelength of 500 nm or a
linear transmittance of 10% or less with the light
having a wavelength of 6.0 μ m.



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ABSTRACT

5 An aluminum nitride sintered body characterized
by comprising aluminum nitride as the main component,
containing a titanium compound, and having a black
color, a transmittance of 10% or less with the light
10 having a wavelength in the range of from 500 to 650 nm
and a heat conductivity of 120 W/m·K or more. The
sintered body is produced by adding 0.05 to 5% by
weight, in terms of Ti, of a titanium compound and a
sintering aid compound and, if necessary, a compound
15 capable of forming carbon after being thermally
decomposed to an aluminum nitride powder, molding the
mixture, heating the molding in vacuo, air or a
nitrogen gas, a hydrogen gas or an atmosphere
comprising a mixture of these gases until the residual
20 carbon content is reduced to 2.0% by weight or less,
and sintering the heat-treated mixture in a
nonoxidizing atmosphere containing nitrogen at 1600°C
or above. The titanium compound is Ti_nO_{2n-1} or a
solid solution comprising Ti_nO_{2n-1} and nitrogen partly
25 dissolved therein in the solid solution form wherein n
is 1 or more, or a compound represented by the formula
 TiN_xO_y wherein $0 < x < 1$ and y is $3/2 (1 - x)$.

There is provided an aluminum nitride sintered
body wherein both the light shielding property and the
25 heat conductivity are stabilized.

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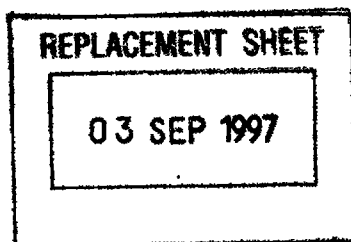
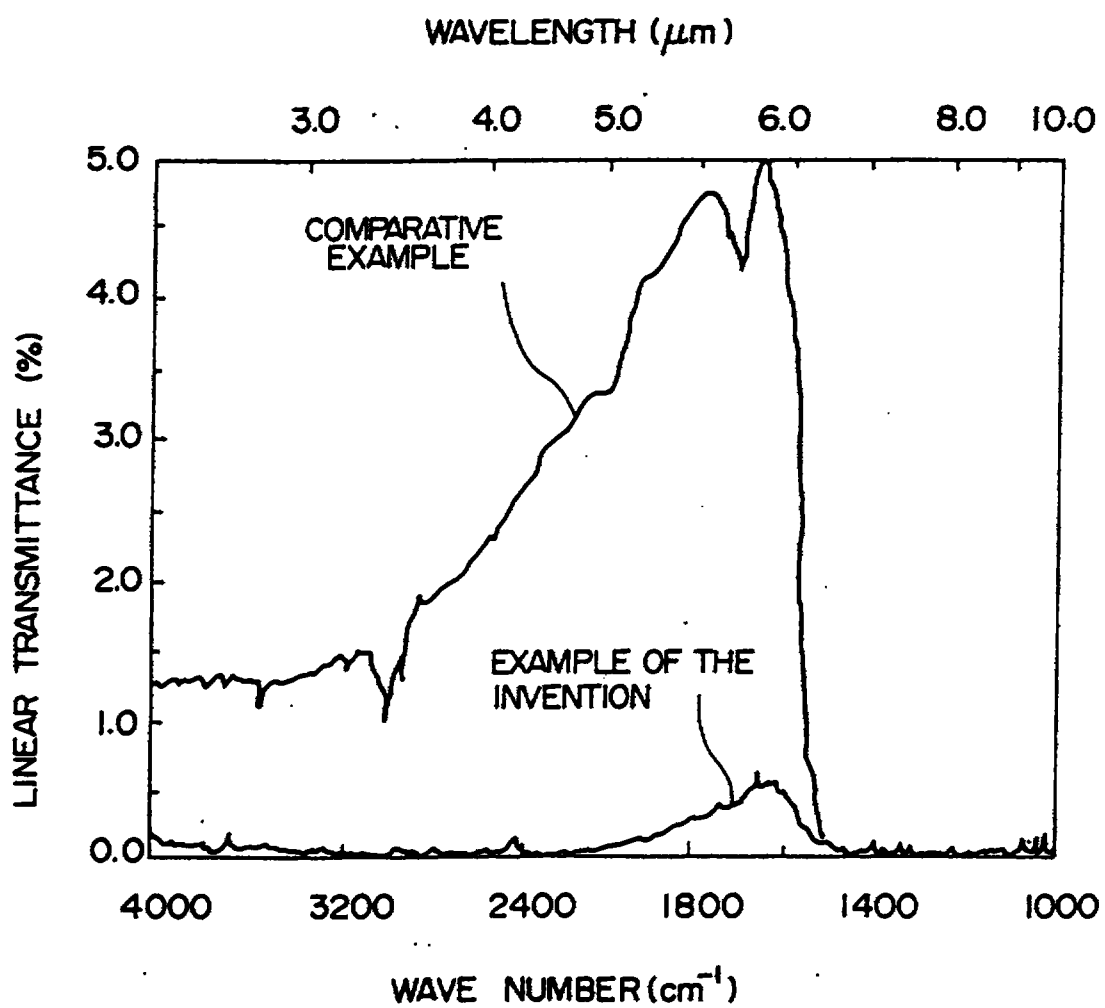


FIG. 1



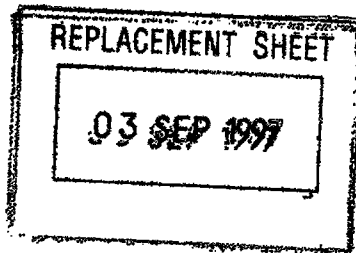
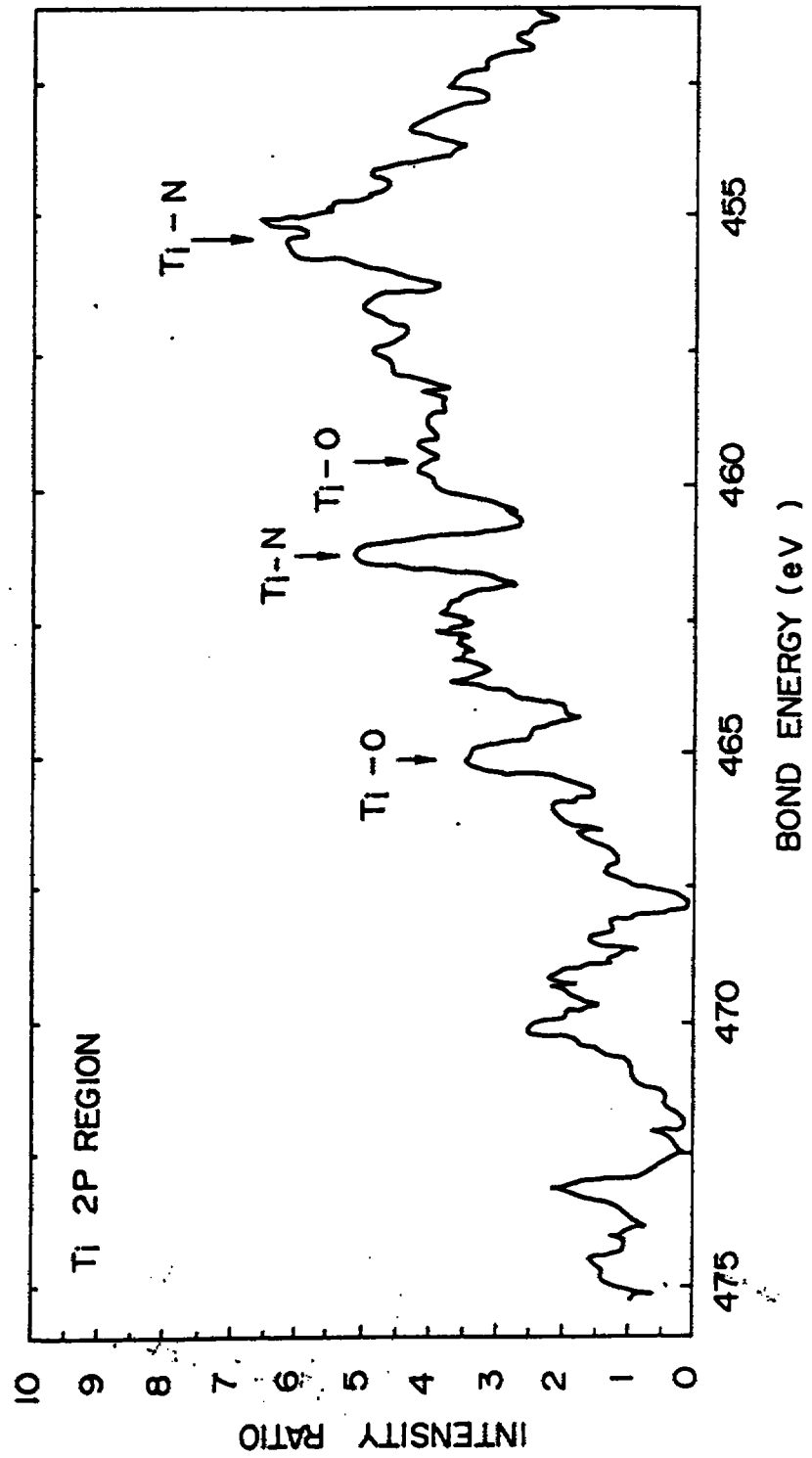


FIG. 2

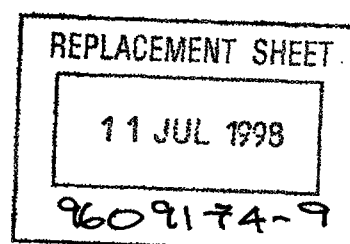


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ABSTRACT

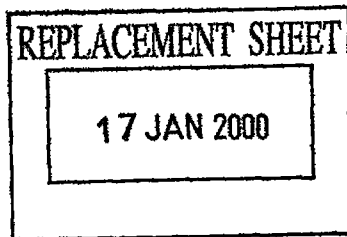
**ALUMINUM NITRIDE SINTERED BODY AND PROCESS
FOR PRODUCING THE SAME**

A sinter which is based on aluminum nitride, contains a titanium compound, is black, and has a transmittance of 10% or less as regards the light with a wavelength of 500 to 650 nm and a thermal conductivity of 120 W/m°K or above. It is produced by molding a mixture of aluminium nitride powder with a titanium compound in an amount of 0.01 to 5 wt% in terms of titanium element, a sintering aid and optionally further a compound which generates carbon by thermal decomposition, heating the molded article in a vacuum, air, nitrogen, hydrogen or a mixture thereof to a residual carbon content of 0.2 wt% or less, and sintering in a nitrogen-containing nonoxidative atmosphere at 1,600°C or above. Examples of the titanium compound to be used include Ti_nO_{2n-1} solid solution comprising Ti_nO_{2n-1} and nitrogen partially dissolved therein, wherein n is 1 or above, and TiN_xO_y wherein $0 < x < 1$ and $y = 3/2 (1-x)$. The obtained sinter has stable light shielding property and thermal conductivity.





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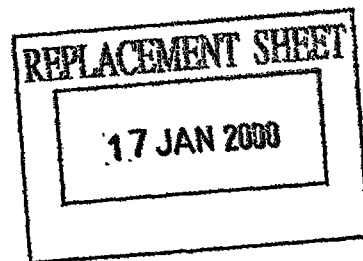


Claims :

- (1) An aluminum nitride sintered body comprising aluminum nitride as the main component, and a titanium compound selected from the group consisting of Ti_nO_{2n-1} , a solid solution comprising Ti_nO_{2n-1} and nitrogen partly dissolved therein in solid solution form, and TiN_xO_y wherein $0 < x < 1$, y is $3/2 (1-x)$, and n is at least 1, said sintered body having a black color, a linear transmittance of not more than 10% for light having a wavelength of 500 to 650nm and a heat conductivity of 120 W/m.K or more.
- (2) A process for producing an aluminum nitride sintered body according to claim 1, characterized by adding 0.01 to 5% by weight, in terms of Ti, of a titanium compound and a sintering aid to an aluminum nitride powder, molding the mixture, heating the molding in vacuo, air, a nitrogen gas, a hydrogen gas or an atmosphere comprising a mixture of these gases until the residual carbon content is reduced to 0.2% by weight or less, and sintering the mixture in a nonoxidizing atmosphere containing nitrogen at 1600°C or above.
- (3) A process according to claim 2, wherein said sintering aid compound comprise at least one compound selected among those of rare earth elements and alkaline earth elements.



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(4) The sintered body according to claim 1, wherein the sintered body has a linear transmittance of 5% or less with the light having a wavelength of 500 nm or a linear transmittance of 10% or less with the light having a wavelength of 6.0 μm .