Titanium alloy complex powder is yielded by hydrogenating titanium alloy raw material to generate hydrogenated titanium alloy, grinding and sifting it to obtain hydrogenated titanium alloy powder, adding ceramic powder selected from SiC, TiC, SiO₂, TiO₂, (here, index x is a real number which is in 1≤x≤2) and Al₂O₃, and dehydrogenating the mixture of the hydrogenated titanium alloy powder and the ceramic powder. In addition, consolidated titanium alloy material is obtained by CIP process and subsequent HIP process to the titanium alloy complex powder or by HIP process after filling the titanium alloy complex powder into capsule.
Fig. 1

Alloy scrap  
Alloy ingot  

↓  
Size control  

↓  
Hydrogenation  

↓  
Grinding·Sifting  

↓  
Hydrogenated alloy powder  

↓  
Mixing  

↓  
Dehydrogenation  

↓  
Adding third component  

Titanium alloy complex powder  

↓  
CIP  

↓  
HIP  

↓  
Titanium alloy material
Fig. 2

Alloy scrap
Alloy ingot

Size control

Hydrogenation

Grinding • Sifting

Dehydrogenation

Titanium alloy powder

Mixing

Adding third component
Titanium alloy complex powder

CIP

HIP

Titanium alloy material
TITANIUM ALLOY COMPLEX POWDER CONTAINING CERAMIC AND PROCESS FOR PRODUCTION THEREOF, CONSOLIDATED TITANIUM ALLOY MATERIAL USING THIS POWDER AND PROCESS FOR PRODUCTION THEREOF

TECHNICAL FIELD

[0001] The present invention relates to titanium alloy complex powder and a process for production thereof, titanium alloy material using this powder, and a process for production thereof, and in particular, relates to titanium alloy material and a process for production thereof using titanium alloy scrap or titanium alloy ingot as a raw material.

BACKGROUND ART

[0002] Titanium alloy, in particular, Ti-6Al-4V alloy has been well known as a material for airplanes. The titanium alloy is produced by a vacuum arc remelting method in which after adding Al—V alloy at an appropriate amount, this is pressed into briquettes, the briquettes are mutually bonded to form an electrode for remelting, the electrode for remelting is set in the vacuum arc remelting furnace, and the electrode is remelted in the vacuum to produce alloy ingots. Alternatively, it can be also produced by an electron beam remelting method in which materials for remelting consisting of titanium material and Al—V master alloy are supplied to a heat source, an electron beam is irradiated on the material to remelt them, and the melted metal is poured into a mold arranged downstream of the heat source to produce alloy ingots.

[0003] However, in the remelting method, there is a problem that even if fine granular raw material of alloy is tried to be dispersed in the heat uniformly, the granular raw materials are sometimes aggregated mutually in the heat and it is difficult to disperse them uniformly.

[0004] Furthermore, in Ti-6Al-4V alloy, since Al—V master alloy which is a raw material is expensive, as a result, cost of titanium alloy ingot produced is increased. To realize further market expansion, a process for production of titanium alloy material which can produce in lower cost compared to a present situation, is required.

[0005] Unlike the above-mentioned remelting method, a powder method can realize a condition in which fine particles are uniformly dispersed after sintered product, as long as raw material powder and fine particles are uniformly mixed.

[0006] However, it is known that the titanium alloy powder has inferior workability and formability compared to pure titanium powder, as a result, there is another problem that sintering density is difficult to be increased. In particular, since Ti-6Al-4V alloy has small plastic deformability, it is known that sintering density is difficult to be increased by an ordinary method by the powder method (See Reference 1 below).

[0007] Therefore, in the powder method of 6Al-4V alloy, the Blended Elemental Powder Metallurgy Process (hereinafter simply referred to as “BE Process”) in which pure titanium powder and Al—40% V alloy powder are used as raw materials instead of using titanium alloy powder, is employed.

[0008] However, since Al—40% V powder, Al powder and V powder which are used in the BE process is very expensive, titanium alloy produced by the powder process will also be very expensive.

[0009] In addition, a dense titanium alloy material has been ordinarily produced by vacuum sintering of solid component consisting of formed powder and by subsequent HIP (Hot Isostatic Press) process. However, since the HIP process generally costs very high in its processing cost, a product produced by the process would be also expensive and such product is limited in a special use.

[0010] Regarding this point, for example, a technique in which inexpensive titanium powder produced by the Hunter method is used in the BE process is known, and reference which discloses that strength and toughness are improved by adding a third component is also known (See References 1 and 2).

[0011] However, upper limit of remaining pores in titanium alloy after sintering is controlled not more than 50 μm in the Reference 2. A titanium alloy having further smaller pore diameter is required in the case in which a material having greater strength than that of the material disclosed in the Reference is required. It is necessary to solve this problem.

[0012] As noted above, there still remains the subject in which sintering density of produced titanium alloy material is difficult to be increased because of remaining voids even in the case in which vacuum sintering and subsequent HIP process of titanium alloy powder are performed.

SUMMARY OF THE INVENTION


[0015] An object of the present invention is to provide titanium alloy complex powder having superior quality by the powder method using titanium alloy scrap or titanium alloy ingot as a raw material, and to provide titanium alloy material and a process for production thereof.

[0016] As a result of the inventors researching about the problems further in view of the above-mentioned circumstances, it was found that titanium alloy complex powder having uniform composition can be produced in low cost, by using the titanium alloy scrap or titanium alloy ingot as a raw material, hydrogenating it to generate hydrogenated titanium alloy, grinding and sifting the hydrogenated titanium alloy to obtain hydrogenated titanium alloy powder, adding a third component to this, and dehydrogenating it to generate titanium alloy powder; or by using the titanium alloy scrap or titanium alloy ingot as a raw material, hydrogenating it to generate hydrogenated titanium alloy, grinding and sifting the hydrogenated titanium alloy to obtain hydrogenated titanium alloy powder, dehydrogenating it to generate titanium alloy powder, and further adding a third component, and thus the present invention has been completed.

[0017] That is, titanium alloy complex powder of the present invention has ceramic powder, and furthermore, the ceramic powder is at least one selected from a group consisting of Si, SiC, SiO, TiO, and AlO. Here, index x is a real number which is in 1≤x≤2.

[0018] In the titanium alloy powder of the present invention, it is desirable that added amount of each ceramic added to the titanium alloy powder is in a range from 0.01 to 0.15 wt %, and the total added amount is in a range from 0.01 to 0.5 wt % in the case in which two or more ceramic powders are added.
In the present invention, it is desirable that particle size of the titanium alloy powder be not more than 150 μm.

In the present invention, it is desirable that the titanium alloy powder raw material contain aluminum and vanadium, or contains at least one kind selected from zirconium, tin, molybdenum, iron and chromium in addition to aluminum and vanadium.

A process for production of titanium alloy powder of the present invention has steps of hydrogenating titanium alloy raw material to generate hydrogenated titanium alloy as a raw material, grinding the hydrogenated titanium alloy as an intermediate material to obtain hydrogenated titanium alloy powder, and as a final step, adding ceramic powder and then dehydrogenating them, or dehydrogenating the hydrogenated titanium alloy powder and then adding and mixing ceramic powder.

In the process for production of titanium alloy material of the present invention, it is desirable that the above noted titanium alloy complex powder be treated by CIP (Cold Isostatic Press) process and subsequent HIP process, or by HIP process after filling the above noted titanium alloy complex powder into a capsule.

Titanium alloy material of the present invention is produced by the above noted process.

Furthermore, in the present invention, it is desirable that ratio of density of the titanium alloy material produced by the above process against the true density be not less than 99%.

As mentioned above, since titanium alloy material of the present invention is produced not via remelting and solidifying, by treating by CIP process and subsequent HIP process, or by treating by HIP process after encapsulating into capsule, distribution of ceramic component can be maintained in uniform and fine condition as originally is added, as a result, titanium alloy material in which ceramic particles are uniformly and finely distributed can be produced, and titanium alloy material having high strength and toughness can be provided in low cost.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a flow chart diagram showing desirable process for production of titanium alloy powder and titanium alloy material of the present invention (ceramic is added before dehydrogenation).

FIG. 2 is a flow chart diagram showing desirable process for production of titanium alloy powder and titanium alloy material of the present invention (ceramic is added after dehydrogenation).

BEST MODE FOR CARRYING OUT THE INVENTION

Preferable embodiments for the present invention are explained below with reference to the drawings.

The titanium alloy complex powder of the present invention is characterized in that ceramic powder is added. It is desirable that the ceramic powder of the present invention be at least one selected from a group consisting of SiC, TiC, SiO₂, TiO₂, and Al₂O₃. Here, index x is a real number which is in 1 ≤ x ≤ 2. It means SiO₂ in the case in which x is 1 and SiO₂ in the case in which x is 2. TiO₂ is determined similarly.

This ceramic powder(s) is/are added to titanium alloy powder at an appropriate amount to obtain titanium alloy complex powder. In the producing process of titanium sintering alloy in which the complex powder is pressed and formed, the ceramic powder is dispersed uniformly in titanium alloy, and as a result, a dispersion-strengthened titanium sintering alloy can be obtained.

Furthermore, not only powdered state of SiC and TiC, but whisker state SiC and TiC can also be used. By adding whisker state SiC and TiC to titanium powder, strength of titanium alloy sintered and produced can be greatly improved. It is desirable that the above noted whisker state SiC and TiC having aspect ratio in a range from 5 to 50 be used.

In addition, among the above noted ceramic powders, SiC and TiC can newly generate TiSi₂ and TiC by reacting with titanium alloy.

As a result, TiSi₂ can improve toughness of titanium alloy. Furthermore, TiC which is generated during forming process has good consistency with titanium alloy matrix. Therefore, conventionally not known effect in which higher strength can be exhibited compared to a case in which TiC is extrinsically added as an alloy element, can be obtained.

As the titanium alloy raw material of the present invention, an alloy scrap or alloy ingot such as titanium alloy chips, titanium alloy forged chips, edge material of titanium alloy rod or the like can be used.

It is desirable that length or dimension of these titanium alloy raw material be controlled in predetermined size beforehand. For example, it is desirable to cut at not more than 100 mm beforehand in the case of alloy chips. By cutting at the above-mentioned length, subsequent hydrogenating process can be efficiently promoted. In addition, in the case of block shaped alloy scrap such as the forged chips, there is no difficulty as long as it has a size which can be put into hydrogenating furnace. In the case in which the alloy raw material is titanium alloy ingot, it is desirable to treat so as to be cut chips having predetermined size by a cutting process.

The titanium alloy raw material treated and controlled as mentioned above, is brought into the hydrogenating process under hydrogen atmosphere. The hydrogenating process is desirably performed at a temperature range from 500 to 650°C. Since hydrogenating process reaction of alloy raw material is exothermic reaction, any heating operation by a heating furnace is not necessary accompanied by promotion of hydrogenating reaction, thus hydrogenating reaction can be promoted automatically.

The alloy as an intermediate material which is hydrogenated treated (hereinafter simply referred to as "hydrogenated titanium alloy") is then cooled to room temperature, and is desirably ground and sifled until hydrogenated titanium powder has predetermined particle size under inert atmosphere such as argon gas or the like. Subsequently, it is desirable to add the ceramic powder of the present invention.

Next, hydrogenated titanium alloy powder in which ceramic powder is added is desirably treated by dehydrogenation process. By heating until it reaches a high temperature range in an atmosphere maintained at reduced pressure, dehydrogenation can be effectively promoted.

The temperature of dehydrogenating process is desirably performed in a range from 500 to 800°C. Since dehydrogenation reaction is endothermic reaction, in contrast to the above-mentioned hydrogenating process reaction, heating operation is necessary until hydrogen is completely generated from hydrogenated titanium alloy powder.
[0040] Titanium alloy powder obtained by the above-mentioned dehydrogenating process is sometimes sintered together, in this case, it is desirable that the grinding and sintering processes be performed again.

[0041] Hydrogenated titanium alloy powder which is ground and sifted until it has predetermined particle size, can be dehydrogenated as it is. It is desirable that ceramic powder of the present invention be added and mixed with titanium alloy powder of which dehydrogenation process is completed. In this case, an ordinary mixing means such as V-type mixing machine or the like can be employed to add and mix.

[0042] As above-mentioned, ceramic powder can be added before or after dehydrogenation process. Aggregation and sintering of titanium alloy powder during dehydrogenation can be prevented and oxygen content in titanium alloy powder can be maintained in low level in the case in which ceramic powder is added before dehydrogenation process. However, load during steps is increased, that is, dehydrogenation furnace and devices for grinding and sintering after dehydrogenation process should be controlled depending on kind of ceramic.

[0043] Dehydrogenation process can be promoted more efficiently in the case in which dehydrogenation process is performed before adding ceramic powder. Furthermore, dehydrogenation furnace and devices for grinding and sintering are easily controlled.

[0044] In the present invention, it is desirable that particle size of the hydrogenated titanium alloy powder after grinding and sintering be controlled in a range from 10 to 150 μm. By controlling in the range, consolidating can be promoted in subsequent consolidating process.

[0045] It is desirable that ceramic powder used in the present invention be at least one selected from a group of particles of SiC, SiO₂, TiO₂, TiC and Al₂O₃. Particle size of the ceramic powder is desirably in a range from 0.01 to 50 μm, more desirably in a range from 0.1 to 20 μm.

[0046] In the case in which ceramic powder is ultra fine particle less than 0.01 μm, particles of the third component may be undesirably aggregated each other during mixing with titanium alloy powder. On the other hand, in the case in which ceramic powder is more than 50 μm, dispersibility is undesirably not sufficient.

[0047] In the present invention, it is desirable that ratio of adding of the ceramic powder be 0.01 to 0.15 wt % in the case in which one kind of SiC, SiO₂, TiO₂, TiC and Al₂O₃ is added. In addition, it is desirable that the total ratio of adding of be 0.01 to 0.3 wt % of in the case in which two kinds or more of these ceramic powders are added. By adding in the range, mechanical properties of titanium alloy of which titanium alloy powder of the present invention is used as a starting material, formed and processed, can be maximally exhibited.

[0048] In the present invention, it is desirable that the consolidating process be performed by combining CIP and HIP appropriately.

[0049] For example, it is desirable that titanium alloy complex powder obtained in the above-mentioned method be filled in a CIP rubber, treated at 100 to 200 MPa, then filled in a HIP capsule, and HIP treated at a temperature not higher than β transformation point at 50 to 200 MPa for 1 to 5 hours without CIP process. Consolidated titanium alloy material can also be obtained by HIP process alone.

[0050] Alternatively, it is desirable that titanium alloy complex powder obtained in the above-mentioned method be filled in a HIP capsule and HIP treated at a temperature not higher than β transformation point at 50 to 200 MPa for 1 to 5 hours without CIP process. Consolidated titanium alloy material can also be obtained by HIP process alone.

[0051] Function and effect of adding each ceramic powder to alloy scrap is exhibited during sintering process.

[0052] Therefore, effect of each ceramic powder of the present invention is explained as below.

Function and Effect of Addition of SiC

[0053] As SiC added to hydrogenated alloy powder, commercially available powdered sample can be used. In the present invention, it is desirable that SiC powder be added in a range from 0.01% to 0.15% of weight of titanium alloy powder. Furthermore, particle size of SiC added is desirably in a range from 0.01 μm to 50 μm, and more desirably in a range from 0.1 μm to 20 μm.

[0054] By controlling within above range, and by CIP process and subsequent HIP process of titanium alloy powder or by HIP process after encapsulating titanium alloy powder into capsule, size and existence frequency of dispersion phase in structure of final product can be desirably controlled without negatively affecting to properties of titanium alloy final product.

[0055] During HIP process, SiC powder added to titanium alloy complex powder reacts with titanium in the matrix as following reaction formula to generate TiC and Si.

\[ \text{SiC} + \text{Ti} \rightarrow \text{TiC} + \text{Si} \] (hereinafter "\rightarrow" means right arrow sign.)

[0056] TiC generated in the above reaction is uniformly dispersed in the matrix with keeping coherency with the matrix in titanium, as a result, tensile strength is also superior compared to a case in which SiC is not added. Of course, there are several particles remaining as SiC in the matrix not completing the above reaction entirely during HIP process period. These remaining particles also contribute to dispersion strengthening.

[0057] Furthermore, in the case in which SiC is added, not only TiC but Si metal is also generated in the matrix. Si metal generated in the matrix reacts with titanium in the matrix to generate TiSi₂.

\[ 2\text{Si} + \text{Ti} \rightarrow \text{TiSi}_2 \]

[0058] TiSi₂ generated in the matrix is deposited with keeping coherency with the matrix phase, and toughness of titanium alloy material can be increased.

Function and Effect of Addition of TiC

[0059] In the present invention, it is desirable to add TiC to the titanium alloy powder. It is desirable that additional ratio of TiC be controlled in a range from 0.01% to 0.15% of weight of titanium alloy powder. Particle size of TiC added is desirably in a range from 0.01 μm to 50 μm, and more desirably in a range from 0.1 μm to 20 μm.

[0060] By controlling within above range, size and existence frequency of dispersion phase in structure of final product can be desirably controlled without negatively affecting to properties of titanium alloy final product of which titanium alloy powder of the present invention is consolidated.

[0061] By CIP process and subsequent HIP process of titanium alloy complex powder having titanium alloy powder and TiC powder or by HIP process after encapsulating them into capsule, consolidated titanium alloy material of the present invention can be obtained.
Size of TiC in titanium alloy material after HIP process is maintained in a range from 0.01 to 50 μm which is a particle size of addition, and its existence frequency is not less than 5 particles/mm². TiC phase uniformly and finely dispersed in the matrix greatly contributes to improve mechanical properties such as tensile strength, fatigue strength or the like by dispersion strengthening.

**Function and Effect of Addition of SiO₂**

As same as in the case of SiC addition, by adding SiO₂ powder which is an example of SiO₂ to titanium alloy powder at 0.01% to 0.15%, and by CIP process and subsequent HIP process or by HIP process after encapsulating into a capsule, mechanical properties of titanium alloy material can be improved. That is, TiO₂ phase which is generated by reacting with titanium phase; SiO₂ phase which is remaining on the middle way of reaction; and TiSi₂ phase which is generated by reaction of Si phase generated as a result of reaction and Ti; all exist in the titanium matrix, they exist uniformly and finely to contribute to increase mechanical strength, and elongation decrease due to addition is controlled.

**During HIP process, SiO₂ powder added to titanium alloy complex powder reacts with titanium in the matrix as following reaction formula to generate TiO₂, Si, and TiSi₂:**

\[
\text{SiO}_2 + \text{Ti} \rightarrow \text{TiO}_2 + \text{Si}
\]

**TiO₂** generated in the above reaction remains in titanium alloy, as a result, dispersion strengthening of titanium alloy itself occurs. Furthermore, TiSi₂ generated in the above reaction contributes to improve toughness of titanium alloy.

**It should be noted that, in the case in which SiO₂ such as SiO or the like is used instead of SiO₂ powder, TiO₂ and Si are generated in a similar way to the above reaction, it reacts with Ti to generate TiSi₂, to contribute to improve toughness of titanium alloy.**

**Function and Effect of Addition of TiO₃**

As same as in the case of TiC addition, by adding TiO₃ powder which is an example of TiO₃ to titanium alloy powder, and by CIP process and subsequent HIP process or by HIP process after encapsulating into a capsule, mechanical properties of titanium alloy material can be improved. Ranges of added amount and desirable particle size of TiO₃ powder are as same as in the case of TiC addition.

**Furthermore, in the case in which TiO₃ such as TiO or the like is added to titanium alloy, mechanical properties of titanium alloy can be improved similarly.**

**Function and Effect of Addition of Al₂O₃**

As same as in the case of TiC addition or TiO₂ addition, by adding Al₂O₃ powder to titanium alloy powder, and by CIP process and subsequent HIP process or by HIP process after encapsulating titanium alloy powder into a capsule, mechanical properties of titanium alloy material can be improved. In this case, since Al₂O₃ particle is stable and does not react with Ti at all, particle size and existence frequency of particles at the time of addition are maintained as they are, and structure controlling of titanium alloy material is little affected by HIP process conditions. Therefore, planning of material becomes easier. Contribution to strength improving by Al₂O₃ phase is caused by a dispersion effect.

**Complex Addition of Ceramic Type Particles (TiC, TiO₂, SiC, SiO₂, Al₂O₃)**

Addition of the ceramic powder of the present invention is not limited in one kind, two or more kinds of powder can be added. In such case, raw material of ceramic powder is desirably in a range from 0.01 to 0.3 wt %. Particle size of each ceramic added is desirably in a range from 0.01 to 50 μm, more desirably in a range from 0.01 to 20 μm. By controlling added amount and particle size within the range, size and existence frequency of ceramic particles in the structure of titanium alloy material of the present invention can be appropriately controlled.

**Titanium alloy complex powder controlled by the above-noted process can be efficiently consolidated by CIP process and subsequent HIP process, or by HIP process after filling titanium alloy complex powder into a capsule.**

**In particular, in the present invention, by appropriately adding ceramic powder selected from SiC, TiC, SiO₂, TiO₂, and Al₂O₃ to titanium alloy powder, effects of dispersion strengthening, crystal particle refinement, improve of tensile strength, and improve of toughness in titanium alloy can be exhibited. In particular, in adding of SiC and SiO₂, in which TiSi₂ is generated, effect of reducing ductility decrease is great.**

**Furthermore, in the present invention, titanium alloy such as Ti-6Al-4V alloy, Ti-3Al-2.5V alloy, Ti-6Al-2Sn-4Zr-6Mo alloy, Ti-6Al-6V-2Sn alloy, Ti-10V-2Fe-3Al alloy (10-2-3), Ti-5Al-4V-0.6Mo-0.4Fe alloy (Timetal 54M), Ti-4.5Al-3V-2Fe-2Mo alloy (SP700), Ti-15V-3Cr-3Al-3Sn alloy (15-3-3-3), Ti-4Al-2.5V-1.5Fe alloy (AT1425), Ti-5Al-5V-5Mo-3Cr alloy (Ti-5553) can be used as the above mentioned raw material of titanium alloy powder.**

**Mechanical properties of titanium alloy material containing copper, chromium or iron and being consolidated by the above-mentioned method can be further controlled by subsequent processing such as rolling, extrusion or drawing and heat process.**

**EXAMPLES**

**Example 1**

**Production of hydrogenated titanium alloy powder** explained below. Scrap cut chips of Ti-6Al-4V alloy were cut into chips having length not greater than 10 mm. The chips were inserted into a container and the container was set in a furnace. After vacuum evacuation inside the furnace, heating was started, hydrogen was induced into the furnace after the temperature inside the furnace reached 300°C, and heating was continued until 650°C while maintaining the inside of the furnace in a slightly pressurized condition by hydrogen. During this process, since Ti-6Al-4V alloy scrap chips and hydrogen are reacted and temperature inside the furnace is increased, heater output was set at 0, and the condition was maintained as it was until the reaction was completed.

**After the reaction was completed, the furnace was allowed to cool and the material was taken out. Confirming was by X-ray diffraction, since only peaks of hydrogenated titanium were detected, and it was confirmed that all the material was converted into hydrogenate. Grinding this hydrogenate under an argon gas atmosphere and sifting by a...
sifter of 300 mesh yielded hydrogenated titanium alloy powder having a particle size not greater than 48 µm.

Example 2

[0077] TiO₂ powder was each added at 0%, 0.05 wt %, 0.1 wt %, 0.15 wt % and 0.5 wt % to hydrogenated titanium alloy powder having composition of Ti-6% Al-4% V of Example 1, to prepare five samples and each mixed by a V-type mixing machine. TiO₂ powder used was a powder produced by oxygen combustion method of TiCl₄, and the average particle size was 0.8 µm.

[0078] Each sample of hydrogenated titanium alloy powder to which TiO₂ was added was inserted into a container made of titanium, and dehydrogenation process was performed in a vacuum heating furnace. Starting heating after vacuum evacuation, dehydrogenation reaction of which hydrogen gas was separated occurred at about 300°C. Heating was continued to increase the temperature up to 500°C, and then 600°C, dehydrogenation was promoted. Since dehydrogenation reaction is an endothermic reaction, it is important to maintain temperature inside of the furnace at a constant level to perform dehydrogenation efficiently. When the temperature was maintained at 650°C for 1 hour, the degree of vacuum was recovered. Since the vacuum degree of 1×10⁻⁵ mbar was obtained, heating was stopped, and cooled. Since powder taken out of the furnace was partially aggregated, it was crushed by a crushing machine to obtain titanium alloy particle not greater than 300 µm.

Example 3

[0079] TiO₂ added titanium alloy powder of Example 2 was filled in a CIP rubber, and CIP treated at 150 MPa. The CIP compact was encapsulated in a soft steel capsule and HIP treated to obtain titanium alloy material of the present invention. The conditions of HIP were 900°C, 100 MPa and 1 hr. After HIP process, titanium alloy material was taken out, its apparent density was measured and the ratio to theoretical density (hereinafter simply referred to as “density ratio”) was calculated. The result is shown in Table 1.

[0080] The density ratio of titanium alloy material is increased from 99.1% to 99.5% in the case in which added amount of TiO₂ is increased from 0.05 wt % to 0.15 wt %.

Example 3-2

[0081] TiO₂ added titanium alloy powder of Example 2 was filled in a soft steel capsule and HIP treated. The conditions of HIP were 900°C, 100 MPa and 1 hr. After HIP process, titanium alloy material was taken out, its density was measured and the density was not less than 99%. Here, the density means the ratio of apparent density against true density.

Example 4

[0082] Tension test of titanium alloy material (TiO₂ added Ti-6Al-4V) of Example 3 was performed. The result is shown in Table 1. In Table 1, results of measuring the density are also shown. There is a tendency that elongation is decreased from 13% to 10% and tensile strength is increased from 1050 to 1100 MPa in the case in which added amount of TiO₂ is increased from 0.05 wt % to 0.15 wt %.

Example 4-2

[0083] Tension test of titanium alloy material (TiO₂ added Ti-6Al-4V) produced in Example 3-2 was performed. The result is shown in Table 1. In Table 1, results of measuring the density are also shown. There is no difference in the density ratio, tensile strength and elongation observed, between the case in which TiO₂ added Ti-6Al-4V alloy powder is encapsulated into capsule and HIP treated and the case in which CIP treated and subsequently HIP treated.

<table>
<thead>
<tr>
<th>TiO₂ added amount (%)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation (%)</th>
<th>Density ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 3/1</td>
<td>0.05</td>
<td>1050</td>
<td>13</td>
</tr>
<tr>
<td>Example 4</td>
<td>0.15</td>
<td>1100</td>
<td>10</td>
</tr>
<tr>
<td>Example 3-2/1</td>
<td>0.05</td>
<td>1050</td>
<td>13</td>
</tr>
<tr>
<td>Example 3-2/2</td>
<td>0.15</td>
<td>1100</td>
<td>10</td>
</tr>
<tr>
<td>Comparative</td>
<td>0.15</td>
<td>900</td>
<td>15</td>
</tr>
</tbody>
</table>

Example 5

[0084] As a result of confirming structure of samples of Example 4 and Comparative Example 1, it was confirmed that TiO₂ phase existed dispersing uniformly in the matrix. Size and existence frequency of TiO₂ phase are as shown in Table 2. Here, size of TiO₂ phase means maximal diameter of TiO₂ phase dispersed in the matrix. In addition, existence frequency of TiO₂ phase means the number of TiO₂ particles confirmed in a unit area of the matrix.

[0085] There is a tendency that the maximal diameter of TiO₂ phase in the matrix of titanium alloy sintered bodies is increased from 5 µm to 15 µm in the case in which added amount of TiO₂ to titanium alloy powder is increased from 0.05 to 0.15%. Furthermore, there is a tendency that the number of TiO₂ particles per a unit area of the matrix is increased from 15 particles/mm² to 40 particles/mm².

Example 6

[0086] Instead of TiO₂ powder of Example 2, SiO₂ powder having size of 2 µm was each added at 0.05 wt %, 0.1 wt %, 0.15 wt % and 0.5 wt % to titanium alloy powder, and CIP process and subsequent HIP process were performed in a manner similar to those of Examples 3 and 4, to obtain titanium alloy material of the present invention. Next, measurement of the density ratio and the tension test of titanium alloy material obtained were performed.
Example 6-2

[0087] SiO₂ added titanium alloy powder of Example 6 was filled in a soft steel capsule and HIP treated. Conditions of HIP were 900°C, 100 MPa, and 1 hr. After HIP process, titanium alloy material was taken out, its density ratio was measured and tensile test was performed.

[0088] As a result, there is a tendency that the tensile strength was increased from 1050 to 1100 MPa and the elongation was decreased from 15% to 13% and in the case in which added amount of SiO₂ is increased from 0.05 to 0.15 wt%. On the other hand, the density ratio is increased from 99.2 to 99.5%. There is no difference in the density ratio, the tensile strength and the elongation observed, in the case of Example 6-2 in which SiO₂ added Ti-6Al-4V alloy powder was encapsulated into capsule and HIP treated.

[0089] Next, crystal structure of titanium alloy material obtained was analyzed to qualify dispersions of dispersion phase.

[0090] As a result, Ti₅Si₂ phase and TiO₂ phase were detected. On the other hand, SiO₂ phase was less than detection sensitivity of the qualitative analysis. The results are shown in Table 3.

<table>
<thead>
<tr>
<th>SiO₂ content (%)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation (%)</th>
<th>Maximal Ti₅Si₂ phase size (µm)</th>
<th>Ti₅Si₂ phase existence frequency (particles/mm²)</th>
<th>Maximal TiO₂ phase size (µm)</th>
<th>TiO₂ phase existence frequency (particles/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 6</td>
<td>0.05</td>
<td>1050</td>
<td>15</td>
<td>4</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1100</td>
<td>14</td>
<td>8</td>
<td>16</td>
<td>15</td>
</tr>
<tr>
<td></td>
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<tr>
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<td>Example 3-A</td>
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<tr>
<td>Example 3-B</td>
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</tr>
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</table>

Comparative Example 3-A

[0095] A sample in which no SiO₂ powder was added to hydrogenated titanium alloy powder of Example 1 was prepared. CIP process and HIP process were performed in a manner similar to those of Examples 3 and 4, and measurement of the density and tensile test were performed. The results are shown in Table 1.

Comparative Example 3-B

[0096] A sample in which SiO₂ was added at 0.5 wt % to hydrogenated titanium alloy powder of Example 1 was prepared. CIP process and HIP process were performed in a manner similar to those of Examples 3 and 4, and measurement of the density and tensile test were performed. The results are shown in Table 1. The elongation was decreased to 2% in the case in which TiO₂ was added at 0.5 wt %.

Comparative Example 2

Comparative Example 1-A

[0091] A sample in which no ceramic powder was added to hydrogenated titanium alloy powder of Example 1 was prepared. CIP process and HIP process were performed in a manner similar to those of Examples 3 and 4, and measurement of the density and tensile test were performed. The results are shown in Table 1.

[0092] The elongation was about 15%; however, the tensile strength was decreased to 900 MPa in the case in which no TiO₂ was added.

Comparative Example 1-B

[0093] A sample in which TiO₂ was added at 0.5 wt % to hydrogenated titanium alloy powder of Example 1 was prepared. CIP process and HIP process were performed in a manner similar to those of Examples 3 and 4, and measurement of the density and tensile test were performed. The results are shown in Table 1. The elongation was decreased to 2% in the case in which TiO₂ was added at 0.5 wt %.

Comparative Example 2

Structure of the sample of Comparative Example 1 in which TiO₂ was added at 0.5 wt % was observed. The result is shown in Table 2.
6. A process for producing titanium alloy complex powder, comprising steps of:
   hydrogenating titanium alloy as a raw material to generate hydrogenated titanium alloy as an intermediate material, grinding the hydrogenated titanium alloy as an intermediate material to obtain hydrogenated titanium alloy powder, and dehydrogenating the hydrogenated titanium alloy powder to generate titanium alloy powder before or after adding ceramic powder.

7. Titanium alloy material comprising:
   the titanium alloy complex powder according to claim 1 as a starting material, wherein the powder is pressed and formed.

8. The titanium alloy material according to claim 7, wherein the density of the titanium alloy material is not less than 99% to the theoretical one.

9. The titanium alloy material according to claim 7, wherein titanium compound is dispersed in the titanium alloy, and the titanium compound is a by-product generated by the reaction of the ceramic powder added and solid solved into the titanium alloy powder.

10. The titanium alloy material according to claim 7, wherein the titanium compound is TiC, TiSi, or TiO.

11. A process for production of titanium alloy material, comprising steps of:
   consolidating the titanium alloy complex powder according to claim 1 by CIP process and subsequent HIP process, or by HIP process after filling the titanium alloy complex powder into a capsule.

* * * * *