

S P E C I F I C A T I O N

COATING MATERIAL FOR PLATINUM MATERIAL, PLATINUM MATERIAL COATED
WITH SUCH COATING MATERIAL, AND GLASS MANUFACTURING APPARATUS

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TECHNICAL FIELD

[0001] The present invention relates to a coating material for covering a platinum material for use in a high-temperature environment, such as in a glass manufacturing apparatus.

10

BACKGROUND ART

[0002] An apparatus (including stir chamber, melter, refiner and others) for manufacture of high-quality glasses such as optical glass and display glass generally uses a platinum material as its constituent material. The platinum material is used as the constituent material for such chambers and vessels because of the following. Platinum has a high melting point and forms no oxide layers in the air, so that the platinum material is little subjected to degradation, deformation and damage during operation of such an apparatus. In addition, it is superior in chemical stability and shows a low tendency to contaminate glass in a molten state. Other than platinum, platinum alloys such as a platinum-rhodium alloy have been widely used for the platinum material (other platinum materials applicable for use in glass industry are described in detail in Prior Art section

25

of Patent Literature 1).

[0003] In glass manufacturing processes, the apparatus is placed in a high temperature environment of over 1,000 °C, generally 1,200 - 1,600 °C, while it is varied depending on the content of the treatment used. Because of the above-described features, the platinum material even in such a high temperature environment can maintain sufficient durability over an extended period of time without a tendency to contaminate a molten glass inside the apparatus.

10 [0004] However, the platinum material in the high temperature environment encounters a problem regarding its behavior on an outer surface of the apparatus. The problem is a vaporization loss that results when platinum in the platinum material produces a gaseous oxide in the form of a platinum oxide (PtO_2). This platinum vaporization loss, in its general use, amounts to several % of a weight of the platinum apparatus and becomes a factor that directly damages strength and stability of the platinum material in a local site of the apparatus where a larger amount of platinum vaporizes. Also, the vaporized platinum deposits on surfaces of refractory and heat-insulating materials disposed to surround the glass manufacturing apparatus. This increases the number of members to be subjected to platinum recovery and refinement. Another loss increases as the expensive platinum material vaporizes and spreads into a space
25 where recovery thereof is difficult to achieve.

[0005] Also in the glass manufacturing apparatus using the platinum member, there has been a problem of formation of bubbles, due to water in a glass, at an interface of the platinum member during glass manufacturing (see, for example, Patent Literature 2). This is believed due to the following. Water in the glass decomposes to produce hydrogen that is subsequently allowed to pass through the platinum member to an outside. As a result, an oxygen-concentrated glass portion is formed at or near the interface of the platinum member, whereby oxygen bubbles are produced.

[0006] In order to solve the problem of bubble formation during the glass manufacturing, Patent Literature 3 proposes provision of a hydrogen-impermeable glass-based film on an outer surface of the platinum member.

However, after the study of the glass-based film disclosed in Patent Literature 3, the inventors of this application have found it insufficient to suppress formation of bubbles during the glass manufacturing.

Patent Literature 1: Japanese Patent Laying-Open No. Hei 10-280070

Patent Literature 2: Japanese Patent Kohyo No. 2001-503008

Patent Literature 3: Japanese Patent Kohyo No. 2004-523449

DISCLOSURE OF THE INVENTION

[0007] It is a first object of the present invention to provide a material suitable for coverage of a platinum material used

in a high-temperature environment.

It is a second object of the present invention to provide a coating material for a platinum material, which can suppress bubble formation that is caused by water in a glass during glass manufacturing.

[0008] Key qualities required for the coating material for a platinum material used at a high temperature are summarized below. First, it does not show the tendency to melt or deform in a high-temperature environment and needs to have a sufficient degree of flexibility to follow deformation of the platinum material as a substrate. When the apparatus is operated or brought to rest, its components experience thermal expansion or shrinkage. Accordingly, the coating material if simply high in strength, i.e., rigid, tends to break as a result of failure to follow their dimensional change. This causes them to deform and lose their functions. Second, the coating material, when made into a film, needs to have a dense film quality and must be nearly free of defect such as pinholes. This is because the presence of such defect leads to damaging of the coating material during use and causes the substrate to contact with an outside air, resulting in the failure to sufficiently reduce a vaporization loss of platinum from the substrate.

[0009] Metal oxides, known as general refractory materials, may be regarded as being applicable from standpoints of strength and stability in a high-temperature environment. However, they

are hard to form a dense film by firing, because of their low flexibility and high melting points, and accordingly does not show the performance contemplated by the present invention.

The inventors of this application investigated suitable
5 constitution of the coating material while taking into account the above-described prior conditions, and conceived a concept of the present invention that a material containing crystalline metal oxides of alumina and silica and a glass component can satisfy the above-described conditions.

10 [0010] They reached this invention through the finding that a coating material containing a refractory material component consisting essentially of alumina and silica and a glass component can effectively suppress bubble formation that is caused by water present in a glass during glass manufacturing.

15 That is, the present invention provides a material for coating a surface of a platinum material made of platinum or platinum alloy. More specifically, it provides a coating material for platinum material, which contains a refractory material component containing alumina and silica and a glass
20 component.

[0011] The coating material of the present invention contains alumina particles, a glass component, silica particles and/or colloidal silica. Hereinafter, technical matters common to the following first through fourth embodiments in accordance with
25 the present invention may be referred to as those of "the present

invention".

In a first preferred embodiment in accordance with the present invention, colloidal silica is used to constitute at least a part of silica. Accordingly, the coating material
5 contains alumina particles, a glass component, colloidal silica and, if necessary, silica particles.

[0012] In the first embodiment in accordance with the present invention, the alumina particles and glass component, either with or without silica particles, may be premixed. That is,
10 the alumina particles and glass component, either with or without silica particles, may be mixed, sintered, ground and then combined with the colloidal silica to provide the coating material.

In the first embodiment in accordance with the present
15 invention, the coating material may preferably be provided in a slurry form. That is, the coating material preferably comprises a slurry containing the alumina particles, glass component, colloidal silica, either with or without silica particles. In the case where the alumina particles and glass
20 component, either with or without silica particles, are mixed, sintered and ground, as described above, the coating material comprises a slurry containing the ground product and colloidal silica.

[0013] Preferably, the slurry contains methylcellulose or
25 other water-soluble polymer as an organic binder. The organic

binder is preferably contained in the amount of 0.5 - 10 parts by weight, more preferably 1 - 5 parts by weight, based on 100 parts by weight of inorganic solids in the slurry.

The slurry-form coating material in the present invention
5 can be coated on a platinum material by a method which comprises applying the slurry onto a surface of the platinum material and then firing the slurry. After the slurry is applied onto the surface of platinum material, the applied slurry is preferably dried at a temperature of 40 - 95 °C. The slurry may be applied
10 onto the surface of platinum material while heated. The slurry is preferably applied by spraying.

[0014] In the present invention, in the case where the coating material is applied onto a surface of the platinum material and then fired, the firing temperature is preferably within the range
15 of 1200 - 1600 °C. An environmental temperature at which the platinum material is used may be utilized to effect firing. In this case, the use temperature means the firing temperature. For example, in the case where a platinum material is used in the glass manufacturing apparatus, a member composed of the
20 platinum material is heated, while a molten glass passes through the member, to a temperature at which a coating material layer applied onto the platinum material is fired.

[0015] In the first embodiment of the present invention, a coating material containing alumina particles, glass component
25 and colloidal silica, either with or without silica particles,

is applied onto a surface of the platinum material and then fired, resulting in obtaining a fired coating film. Since colloidal silica is used as at least a part of silica, the colloidal silica serves as an inorganic binder. Accordingly, the fired coating film in the first embodiment can be made sufficiently dense to prevent passage of hydrogen and, as a result, effectively suppresses bubble formation in a glass during manufacturing of the glass. The formation of this fired coating film in the first embodiment is particularly preferred in uses where hydrogen impermeability is needed. It also effectively reduces a platinum vaporization loss.

[0016] After the firing, the colloidal silica consisting of fine particles becomes indiscernible from the glass component as if it vanishes in the glass component. Accordingly, in such a fired coating film, the alumina particles are dispersed in a matrix phase consisting of the glass component and colloidal silica component to constitute a dispersed phase. In the case where the silica particles are contained in the coating material, the silica particles are also dispersed to participate with the alumina particles in the dispersed phase.

[0017] The fired coating film in accordance with the first embodiment of the present invention preferably has a thickness of 100 - 1,000 μm , more preferably 200 - 1,000 μm , further preferably 500 - 1,000 μm . If the thickness of the fired coating film is excessively small, its hydrogen impermeability may become

insufficient. On the other hand, if excessively large, the effect proportional to the thickness is not obtained to become economically disadvantageous.

[0018] The alumina particles for use in the present invention
5 preferably have a mean particle diameter in the range of 1 - 100 μm , more preferably in the range of 3 - 80 μm . In the case where silica is used in the form of silica particles, they preferably have a mean particle diameter in the range of 1 - 100 μm , more preferably in the range of 3 - 80 μm . If the mean
10 particle diameter is excessively large, the coating material even if containing the glass component may fail to provide a dense film. On the other hand, if the mean particle diameter is excessively small, they may fail to serve as a filler that imparts strength to a resulting film.

15 [0019] In the case where silica is used in the form of colloidal silica, it preferably has a mean particle diameter in the range of 10 - 100 nm, more preferably in the range of 10 - 50 nm, further preferably in the range of 10 - 30 nm. In the coating material, the colloidal silica acts as an inorganic binder, as described
20 above. Accordingly, the use of colloidal silica results in the formation of a dense coating film.

[0020] The type of the glass component for use in the present invention is not particularly specified. However, the glass component is expected to be alkali-free when it is applied to
25 an alkali-free glass manufacturing apparatus. In the light of

the absolute requirement that an alkali component should be prevented from entering a glass (product) inside a platinum apparatus even if cracks are produced therein, it is preferred that the glass component constituting the coating material is
5 alkali-free. By "alkali-free" in the present invention, it is meant that the alkali component content does not exceed 0.1 % by weight. Examples of glass components include borosilicate glass and aluminoborosilicate glass.

[0021] In the present invention, the coating material
10 preferably contains 20 - 70 % by weight of a glass component, 15 - 55 % by weight of alumina and 10 - 50 % by weight of silica, on a solid content basis. More preferably, it contains 30 - 70 % by weight of a glass component, 15 - 45 % by weight of alumina and 10 - 30 % by weight of silica, on a solid content basis.
15 Even in the case where colloidal silica is used, a total silica content preferably falls within the above-specified range.

[0022] The content of each component in the coating material may preferably be varied depending on the use temperature of the coating material. As will be described later, in the glass
20 manufacturing facilities, the platinum material is located in roughly three different temperature regions; 1,000 - 1,250 °C, 1,250 - 1,450 °C and 1,450 - 1,600 °C. In the 1,000 - 1,250 °C temperature region, the coating material preferably contains 35 - 70 % by weight (more preferably 40 - 65 % by weight) of
25 a glass component, 10 - 40 % by weight (more preferably 15 -

35 % by weight) of an alumina component and 10 - 50 % by weight (more preferably 10 - 30 % by weight, further preferably 15 - 25 % by weight) of a silica component. In the 1,250 - 1,450 °C temperature region, the coating material preferably contains
5 20 - 60 % by weight (more preferably 25 - 45 % by weight) of a glass component, 20 - 60 % by weight (more preferably 30 - 55 % by weight) of an alumina component and 10 - 50 % by weight (more preferably 10 - 30 % by weight, further preferably 15 - 25 % by weight) of a silica component. In the 1,450 - 1,600 °C
10 temperature region, the coating material preferably contains 15 - 40 % by weight (more preferably 15 - 35 % by weight) of a glass component, 35 - 70 % by weight (more preferably 40 - 65 % by weight) of an alumina component and 10 - 50 % by weight (more preferably 10 - 30 % by weight, further preferably 15 -
15 25 % by weight) of a silica component.

[0023] In a preferred second embodiment of the coating material in accordance with the present invention, silica is used in the form of particles. The glass and alumina components useful in this embodiment are similar in type to those described in the
20 preceding first embodiment.

In the second embodiment in accordance with the present invention, the coating material may take the form of a slurry, paste or green sheet. The coating material, if rendered into the paste or green sheet form, can provide a thick coating film.
25 [0024] In the second embodiment in accordance with the present

invention, alumina particles, silica particles and a glass component may be premixed and sintered. That is, a mixture of alumina particles, silica particles and a glass component may be sintered and then ground to prepare the coating material.

5 [0025] The paste or green sheet in the second embodiment of the present invention contains alumina particles, silica particles and a glass component. As described above, these particles may be mixed, sintered and then ground before they are contained in the paste or green sheet.

10 In the second embodiment in accordance with the present invention, the paste or green sheet preferably contains alumina in the form of fibrous particles (alumina fibers). When the paste or green sheet is applied onto a surface of a platinum material and fired to provide a fired coating film, inclusion
15 of such alumina fibers in the paste or green sheet suppresses production of cracks or the like in the fired coating film. The alumina fibers preferably constitute 0.1 - 30 % by weight of a solid content of the paste or green sheet. The alumina fibers contain Al_2O_3 in the amount of at least 50 % by weight, preferably
20 70 % by weight, and have a length of 0.1 - 100 mm, preferably 1 mm - 50 mm, with a diameter of 0.1 μm - 50 μm , preferably 1 - 20 μm . If the Al_2O_3 content is below 50 % by weight, the heat resistance of the fibers is lowered to such an extent that they readily reacts with the glass component. As a result, the effect
25 of using alumina in the form of fibers can not be expected. If

the fiber length is below 0.1 mm, the fibers simply act in a manner similar to other forms of particles. On the other hand, if it exceeds 50 mm, uniform mixing of such fibers with other components is made difficult. If the fiber diameter is below 5 0.1 μ m, sufficient heat resistance can not be expected. On the other hand, if it exceeds 50 μ m, uniform dispersion of such fibers is made difficult.

[0026] In the second embodiment in accordance with the present invention, the paste or green sheet may further contain a 10 water-soluble polymer, such as methylcellulose, as an organic binder. This organic binder is preferably contained in the range of 0.5 - 10 parts by weight, more preferably 1 - 5 parts by weight, based on 100 parts by weight of inorganic solids in the paste or green sheet.

15 The coating material in the second embodiment of the present invention may take the form of a slurry. This slurry is the one which contains the alumina particles, silica particles and glass component in a mixed form.

[0027] A coating method in accordance with the second embodiment 20 of the present invention is characterized as comprising coating or adhering the coating material in accordance with the second embodiment of the present invention on a surface of a platinum material and then firing the applied coating material.

The firing temperature and other conditions used in the 25 first embodiment also apply to this case.

[0028] The fired coating film in accordance with the second embodiment of the present invention is characterized in that it is obtained by coating or adhering the coating material in accordance with the second embodiment of the present invention on a surface of a platinum material and then firing the applied coating material.

The fired coating film in accordance with the second embodiment of the present invention has the structure in which the alumina particles and silica particles are dispersed, as a dispersed phase, in a matrix phase comprising the glass component. Figure 1 schematically shows the fired coating film in the second embodiment of the present invention. Figure 1(a) shows the fired coating film obtained via firing at a relatively low temperature around 1,300 °C. The alumina particles and silica particles are dispersed in the matrix comprising the glass component. Figure 1(b) shows the fired coating film obtained via firing at a high-temperature region that exceeds 1,500 °C. The alumina particles and silica particles which constitute the dispersed phase are partly dissolved in the matrix phase, so that the matrix phase is made up of the glass component rich in alumina and silica. This improves thermal stability of the matrix phase and accordingly allows the coating material to retain flexibility at a high temperature over 1,500 °C. As a result, it can be coated in a good condition on a substrate without the occurrence of deformation and sagging.

[0029] The fired coating film obtained using the paste or green sheet in accordance with the second embodiment of the present invention preferably has a thickness in the range of 1 - 10 mm, more preferably in the range of 2 - 5 mm. The fired coating
5 film obtained using the slurry has the same thickness as that obtained in the preceding first embodiment.

A preferred third embodiment in accordance with the present invention is characterized in that the slurry in the first embodiment of this invention is coated over a surface of a platinum
10 material to form a slurry coating material layer and then the paste or green sheet in accordance with the second embodiment of this invention is adhered onto the slurry coating material layer to form a protective coating material layer.

[0030] A coating method in accordance with the third embodiment
15 of the present invention is characterized as comprising forming the slurry coating material layer and forming the protective coating material layer thereon, in the fashion as described above, followed by firing the layers. The firing temperature and other firing conditions in the first embodiment of this invention are
20 similarly used.

The slurry coating layer portion (fired slurry coating layer) of the fired coating film in accordance with the third embodiment of this invention preferably has a thickness in the range of 100 - 1,000 μm , more preferably in the range of 200
25 - 1,000 μm , further preferably in the range of 500 - 1,000 μm .

Also, the protective coating layer portion (fired protective coating layer) of the fired coating film preferably has a thickness in the range of 1 - 10 mm, more preferably in the range of 2 - 5 mm.

5 [0031] Illustrating a condition of the fired slurry coating layer in the third embodiment of the present invention, the alumina particles are dispersed as a dispersed phase in a matrix phase comprising the glass component and the colloidal silica component. Illustrating a condition of the fired protective
10 coating layer, the alumina particles and silica particles are dispersed as a dispersed phase in a matrix phase comprising the glass component.

The fired coating film in accordance with the third embodiment of this invention includes the fired slurry coating
15 layer analogous to the fired coating film in accordance with the first embodiment of this invention and the overlying fired protective coating layer having a larger film thickness. Because the fired slurry coating layer which directly covers a platinum material is analogous to the fired coating film in
20 the first embodiment of this invention, it excels in hydrogen permeability and is thus able to effectively suppress bubble formation in a glass during glass manufacturing. The overlying, fired protective coating layer, because of its large film thickness, is able to effectively protect the platinum material
25 in the high-temperature environment and suppress a vaporization

loss of platinum.

[0032] The firing temperature and other conditions used in the first embodiment also apply to this embodiment. Preferably, subsequent to provision of the protective coating material layer
5 on the slurry coating material layer, they are fired simultaneously.

Also in the third embodiment of this invention, the slurry coating material layer and protective coating material layer may contain substantially the same or different proportions of
10 the glass component, silica component and alumina component.

[0033] A fourth embodiment in accordance with this invention is characterized in that the coating material has a two-layer structure having a first coating layer to be brought in contact with a platinum material and a second coating layer overlying
15 the first coating layer, and that the first coating layer comprises a mixture of alumina and silica and the second coating layer comprises a glass component.

In the fourth embodiment of this invention, a fired coating film is obtained by firing the aforesaid coating material having
20 a two-layer structure. A firing temperature and other firing conditions used in the preceding first embodiment also apply to this embodiment. The provision of the fired coating film in the fourth embodiment is primarily contemplated to suppress a platinum vaporization loss in a high-temperature environment.
25 The mixture of alumina and silica, which constitutes the first

coating layer, fulfills a basic function of the coating material, i.e., suffers no damage in a high-temperature environment to cover a platinum material as a substrate. The second coating layer comprising the glass component covers the first coating layer to increase protection of the substrate from contact with the outside air. The second coating layer, while maintaining flexibility even in the high-temperature environment, covers and holds the first coating layer to thereby prevent separation of the first coating layer.

10 [0034] Figure 2 is a schematic view, showing the fired coating film in the fourth embodiment of this invention. As shown in Figure 2(a), when firing is achieved at a temperature of about 1,300 °C, the fired coating film sustains the two-layer structure to cover the substrate. However, when firing is achieved at a temperature exceeding 1,500 °C, the first and second coating layers react with each other so that they are converted to a single-layer form, instead of the two-layer form. As a result, the fired coating film is obtained which comprises the glass component containing high concentrations of alumina and silica.

15 20 [0035] In the fourth embodiment of this invention, the mixed layer (first coating layer) containing alumina and silica preferably comprises 15 - 88 % by weight of alumina and 12 - 85 % by weight of silica. If the alumina content exceeds 88 % by weight, a possibility of producing a defect increases when the first coating layer is caused to react with a glass phase

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at a high temperature of over 1,500 °C. On the other hand, if the silica content exceeds 85 % by weight, the thermal expansion coefficient decreases to increase the occurrence of separation of the first coating layer. The glass component layer (second
5 coating layer) may comprise a single type of glass. It may alternatively comprise a mixture of plural types of glasses. Preferably, a ratio in amount of a glass constituting the second coating layer to the alumina-silica mixed layer is roughly 1:1. If the glass phase becomes excessive, an excess glass component
10 is produced when it reacts in a high-temperature environment. Then, sagging due to this excess glass component may occur. [0036] The first coating layer preferably has a thickness of 50 - 500 µm, particularly preferably 50 - 250 µm. The second coating layer preferably has a thickness of 50 - 500 µm,
15 particularly preferably 50 - 250 µm. If a total thickness of the first and second coating layers is below 100 µm, they may not be made into a dense film that satisfies an anti-oxygen requirement. If it exceeds 1,000 µm, there is an increasing possibility that they may be separated or removed from the
20 substrate when a marked temperature variation occurs. [0037] As described above, the coating material of this invention consists essentially of alumina, silica and a glass component. However, it may further contain a ceramic component, such as zirconia, titania or mullite, when needed.

25 In the present invention, the type of the platinum material

as a substrate is not particularly specified. Other than pure platinum, platinum alloys are also applicable. Examples of platinum alloys include platinum-rhodium, platinum-gold, platinum-palladium, platinum-iridium and platinum-ruthenium alloys. In addition to being applicable to solid solution alloys, the coating material of this invention is applicable to oxide dispersion strengthened platinum alloys, called strengthened platinum.

[0038] The platinum material of the present invention is a platinum material composed of platinum or a platinum alloy and characterized in that it is either coated with the coating material or having on its surface the fired coating film in accordance with the first, second, third or fourth embodiment of this invention. The platinum material coated with the coating material, as described above, refers to a platinum material in condition after the coating material is coated thereon by coating or adhering but before it is fired. The platinum material having on its surface the fired coating film, as described above, refers to a platinum material in condition after the coated coating material is fired.

[0039] The glass manufacturing apparatus of the present invention is characterized as comprising a platinum material either coated with the coating material or having on its surface the fired coating film in accordance with the first, second, third or fourth embodiment of this invention. Likewise with

those aforesaid, the glass manufacturing apparatus comprising a platinum material coated with the coating material refers to the one in condition before the coating material is fired, and the glass manufacturing apparatus comprising a platinum material
5 having on its surface the fired coating film refers to the one in condition after the coating material is fired.

[0040] In accordance with the present invention, superior high-temperature properties of a platinum material can be maintained, while avoiding a vaporization loss of platinum even
10 in a high-temperature environment over 1,000 °C.

Furthermore, in accordance with the present invention, bubble formation can be suppressed during glass manufacturing.

BRIEF DESCRIPTION OF THE DRAWINGS

[0041] [Figure 1] Figure 1 is a view which schematically shows
15 an example of a fired coating film in accordance with a second embodiment of the present invention.

[Figure 2] Figure 2 is a view which schematically shows an example of a fired coating film in accordance with a fourth embodiment of the present invention.

20 [Figure 3] Figure 3 is a view which shows an exemplary construction of a glass manufacturing apparatus.

[Figure 4] Figure 4 is a photograph which shows the condition of interfacial bubbles of Example 6.

[Figure 5] Figure 5 is a photograph which shows the condition
25 of interfacial bubbles of Comparative Example 2.

[Figure 6] Figure 6 is a photograph which shows the condition of interfacial bubbles of Comparative Example 3.

[Figure 7] Figure 7 is a photograph which shows the condition of interfacial bubbles of Comparative Example 4.

5 **EXPLANATION OF REFERENCE NUMERALS**

[0042] 1 ... glass manufacturing facilities

2 ... melter

3 ... refiner

4 ... stir chamber

10 5 ... forming apparatus

6, 7 and 8 ... connecting flow path

BEST MODE FOR CARRYING OUT THE INVENTION

[0043] Examples in accordance with the present invention, together with Comparative Examples, are described below.

15 (Examples 1 - 4 and Comparative Example 1)

The following Examples utilize a slurry-form coating material in accordance with the first embodiment of the present invention.

[0044] Here, a coating material (fired coating film) including
20 a matrix phase of a glass component and a dispersed phase of alumina and silica was placed on a platinum alloy substrate and then the presence of a vaporization loss of platinum from the substrate was examined. In this embodiment, four types of coating materials was prepared containing different ratios in
25 amount of those components. First, a raw material sol (slurry)

having a composition in correspondence to each coating material was prepared.

[0045] The raw material sol (slurry) used alumina and silica in the condition (colloidal silica) of a deionized colloidal solution (alkali-free). As in this embodiment, at least one of alumina and silica which constitutes a dispersed phase is preferably provided in the form of a colloidal solution. As the glass component, an alkali-free aluminoborosilicate glass manufactured by Nippon Electric Glass Co., Ltd. (designated as OA-10 and having a composition comprising, by weight, 60 % SiO_2 , 10 % B_2O_3 , 15 % Al_2O_3 ,

[0046] 5 % CaO , 5 % SrO and 2 % BaO), and an alkali-free aluminoborosilicate glass manufactured by Nippon Electric Glass Co., Ltd. (designated as EF and having a composition comprising, by weight, 55 % SiO_2 , 6 % B_2O_3 , 14 % Al_2O_3 , 24 % $\text{CaO} + \text{MgO}$) were used. The raw material sol (slurry) was prepared by suspending the colloidal solution of glass, alumina and silica in water weighing twice the solid weight, and further adding methylcellulose in the amount of 3 % by weight, based on the solid weight.

[0047] A flat plate (size: 75 mm square x 1.0 mm) made of a Pt-10 wt.% Rh alloy was used as a substrate test piece. The test piece was heated at its back side by a hot air gun. Concurrently, the raw material sol while stirred by a stirrer was supplied to a spray nozzle from which the sol was sprayed

repeatedly over the test piece to a thickness of 200 μm . After application to both sides of the test piece, the sol was fired in a electric furnace to form a coating material (fired coating film).

5 [0048] For the test piece coated with the coating material (fired coating film), the presence of a platinum vaporization loss of platinum was examined. This examination was carried out by heating each test piece at 1,300 $^{\circ}\text{C}$ and 1,500 $^{\circ}\text{C}$ for 100 hours in an outside air and measuring a change in weight thereof after
10 the heating. The results are shown in Table 1. In Table 1, the examination results for the Pt-10 wt.% Rh alloy without the coating material (fired coating film) are also shown.

[0049] [TABLE 1]

	Composition (wt%)				Platinum Vaporization Loss	
	Al_2O_3	SiO_2	Glass Component		1300 $^{\circ}\text{C}$	1500 $^{\circ}\text{C}$
			OA-10	BF		
Ex. 1	15.9	14.1	35.0	35.0	0	0
Ex. 2	26.5	23.5	50	-	0	0
Ex. 3	36.5	23.5	40	-	0	0
Ex. 4	39.0	23.5	37.5	-	0	0
Comp. Ex. 1 (Pt-Rh Alloy)	-	-	-	-	0.12g	0.35g

15 [0050] As can be seen from Table 1, no platinum vaporization loss occurred in the platinum alloy coated with the coating material (fired coating film). This confirms that the coating material has a superior protective effect. The same effect has also been confirmed at a high temperature over 1,500 $^{\circ}\text{C}$. On the

other hand, it has been confirmed that, without the coating material (fired coating film), the platinum alloy shows a platinum vaporization loss of at least 0.1 g, both at 1,300 °C and 1,500 °C, and its amount increases as the temperature is
5 further elevated.

[0051] (EXAMPLE 5)

This Example conforms to the fourth embodiment of the present invention.

In this Example, a coating material (fired coating material)
10 having a two-layer structure was manufactured. First, a raw material sol (slurry) containing alumina and silica (53.1 % by weight of alumina and 46.9 % by weight of silica) was coated onto a substrate. The same solvent and preparation method were used as in Examples 1 - 4. Only loadings thereof were adjusted.
15 As similar to Examples 1 - 4, the raw material sol was spray coated. The coated sol was dried and then fired to form a first coating layer (150 μm thick).

[0052] Thereafter, a second coating layer was formed on the first coating layer. This second coating layer was made of a
20 glass component layer containing 50 % by weight of an OA-10 glass component and 50 % by weight of an EF glass component. In the forming process of the second coating layer, the sol was spray coated to a film thickness of 150 μm, as described above.

The resulting test piece carrying the coating material
25 (fired coating film) thereon was then subjected to the same method

as used in Examples 1 - 4 to examine the presence of a platinum vaporization loss. The results are shown in Table 2.

[0053] [TABLE 2]

	Coating Material Composition (wt%)				Platinum Vaporization Loss	
	First Coating Layer		Second Coating Layer		1300°C	1500°C
	Al ₂ O ₃	SiO ₂	OA-10	EF		
Ex. 5	53.1	46.9	35.0	35.0	0	0
Comp. Ex. 1 (Pt-Rh Alloy)	-	-	-	-	0.12g	0.35g

5 [0054] As evident from Table 2, no platinum vaporization loss occurred in the platinum alloy coated with the coating material (fired coating film), as similar to Examples 1 - 4. This coating material (fired coating film) has been found to maintain its two-layer structure at 1,300 °C but change into a single layer
10 at 1,500 °C. It has been confirmed, however, that the protective effect of the coating material is sustained even at 1,500 °C.

[0055] (EXAMPLE 6 and COMPARATIVE EXAMPLES 2 - 4)

This Example conforms to the first embodiment of the present invention.

15 A slurry containing a glass component, Al₂O₃, SiO₂ and ZrO₂ was prepared according to the composition specified in Table 2. OA-10 (mean particle diameter of 7 μm) was used as the glass component. Al₂O₃ was used in the form of alumina particles (mean particle diameter of 50 μm). SiO₂ was used in the form of
20 colloidal silica (colloidal solution of silica, mean particle

diameter of 20 nm). ZrO_2 was used in the form of zirconia particles (mean particle diameter of 6 μm). These components were suspended in water weighing twice the solid weight. Then, methylcellulose was added in the amount of 3 % by weight, based
5 on the solid weight, to prepare the slurry.

[0056] [Application of slurry to platinum crucible]

While an interior surface of a sand-blasted platinum crucible (46 mm in diameter and 40 mm in height) was heated by a hot air gun, the slurry was spray coated on exterior bottom
10 and side surfaces of the platinum crucible. The coating on the side surface extended upwardly from the bottom surface to a height of 25 mm. After dried at 80 $^{\circ}\text{C}$, the crucible was fired at 1,500 $^{\circ}\text{C}$ for 5 hours to fire the coating material layer. This resulted in obtaining a 500 μm thick, fired coating film.

15 [0057] [Interfacial bubble formation test]

After the coating material was fired, the platinum crucible was cooled to 1,300 $^{\circ}\text{C}$, filled with an aluminoborosilicate glass (OA-10), elevated in temperature to 1,500 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ and then maintained at 1,500 $^{\circ}\text{C}$ for 1 hour.

20 The condition of interfacial bubbles was evaluated by the rating O if no or little bubbles were observed and by the rating X if many bubbles were observed. The evaluation results are shown in Table 3.

[0058] The condition of interfacial bubbles in the platinum
25 crucible was shown in Figures 4 - 7 by photographs. Figure 4

corresponds to Example 6, Figure 5 to Comparative Example 2, Figure 6 to Comparative Example 3 and Figure 7 to Comparative Example 4.

[0059] [TABLE 3]

		Ex. 6	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Compo- sition (wt%)	Glass Component(0A-10)	25.0	25.0	25.0	25.0
	Al ₂ O ₃	51.5	75.0	-	-
	SiO ₂	23.5	-	75.0	23.5
	ZrO ₂	-	-	-	51.5
	Total	100	100	100	100
Condition of Interfacial Bubbles		○	×	×	×

5

[0060] As can be clearly seen from the results shown in Table 3 and Figures 4 - 7, the platinum crucible of Example 6 coated with the coating material containing Al₂O₃ and SiO₂ as essential components other than the glass component shows a marked

10 reduction of bubbles, compared to that coated with the coating material which, other than the glass component, contains Al₂O₃ only in Comparative Example 2, SiO₂ only in Comparative Example 3, or SiO₂ and ZrO₂ in Comparative Example 4. This demonstrates that, in order to suppress formation of bubbles during glass

15 manufacturing, it is necessary to incorporate alumina and silica as essential components, in accordance with the present invention.

It has been also found that the coating material of this Example can reduce a platinum vaporization loss, as similar to

20 those of Examples 1 - 5.

[0061] (EXAMPLES 7 - 9)

These Examples conform to the first embodiment of the present invention.

Slurry solutions of Examples 7 - 9 were prepared having the compositions specified in Table 4. The same types of glass component, Al_2O_3 and SiO_2 as used in Example 6 were used.

[Application of coating material to platinum crucible]

While an interior surface of a sand-blasted platinum crucible (46 mm in diameter and 40 mm in height) was heated by a hot air gun, each slurry was spray coated on exterior bottom and side surfaces of the platinum crucible, as similar to Example 6. Coating was achieved such that the coating layer after fired formed a 500 μm thick film. The coated slurry was dried at 80 $^{\circ}\text{C}$ to form a slurry coating material layer.

[0062] The platinum crucible on which the slurry coating layer was formed in the manner as described above was then fired at a test temperature for 5 hours, cooled to a temperature 200 $^{\circ}\text{C}$ lower than the test temperature, filled with an aluminoborosilicate glass (OA-10), elevated in temperature to the test temperature specified in Table 4 for Examples 7 - 9 at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ and then maintained at the test temperature for 1 hour. The condition of interfacial bubbles is shown in Table 4.

[0063] [TABLE 4]

	Composition (wt %)			Test Temp.	Condition of Interfacial Bubbles	Use Temperature Region
	Al ₂ O ₃	SiO ₂	Glass Component (OA-10)			
Ex. 7	26.5	23.5	50.0	1200°C-1 hr.	○	1000~1250°C
Ex. 8	39.0	23.5	37.5	1300°C-1 hr.	○	1250~1450°C
Ex. 9	51.5	23.5	25.0	1500°C-1 hr.	○	1450~1600°C

[0064] As can be clearly seen from the results shown in Table 4, the application of the coating material containing Al₂O₃ and SiO₂ as essential components other than the glass component, as in Examples 7 - 9, suppresses bubble formation during glass manufacturing. As also shown in Table 4, the heat resistance to endure in a higher use temperature region can be imparted to the coating material by reducing its glass component content and increasing its alumina component content.

It has been also found that the coating materials of these Examples can reduce a platinum vaporization loss, as similar to those of Examples 1 - 5.

[0065] (EXAMPLE 10)

This Example uses a paste-form coating material in accordance with the second embodiment of the present invention.

A mixture containing 37.5 % by weight of a glass component (OA-10), 39.0 % by weight of alumina (Al₂O₃) particles and 23.5 % by weight of silica (SiO₂) particles, as shown in Table 5, was first sintered to provide a sintered body. The silica particles had a mean particle diameter of 20 μm. The alumina particles were the same particles as used in Example 6. Sintering was

performed at 1,500 °C for 24 hours. The obtained sintered body was ground to provide a ground product having a mean particle diameter of about 20 μm.

[0066] 100 parts by weight of the ground product obtained and
5 5 parts by weight of alumina fibers (97 wt.% Al₂O₃-3 wt.% SiO₂, mean fiber length = 10 mm, mean fiber diameter = 3 μm) were added to an aqueous solution containing a methylcellulose resin dissolved therein at a concentration of 9 % by weight. The resultant was mixed to prepare a paste. The aqueous solution
10 containing the methylcellulose resin was added in the amount of 40 parts by weight, based on 100 parts by weight of the aforementioned ground product and alumina fibers.

[0067] [Adhesion of paste to platinum crucible]

The above paste was adhered onto exterior bottom and side
15 surfaces of a sand-blasted platinum crucible (46 mm in diameter and 40 mm in height). The adhered paste covered the same regions of the platinum crucible as in Example 6. After adhesion of the paste, the platinum crucible was fired at 1,500 °C for 5 hours, cooled to 1,300 °C, filled with an aluminoborosilicate
20 glass (OA-10), elevated in temperature to 1,500 °C at a heating rate of 10 °C/min and then maintained at 1,500 °C for 1 hour. The condition of interfacial bubbles is shown in Table 5.

[0068] [TABLE 5]

	Ex. 10
OA-10 (Powder)	35.7wt% (37.5wt%)
Al ₂ O ₃ (Powder)	37.1wt%(39.0wt%)
SiO ₂ (Powder)	22.4wt%(23.5wt%)
97%Al ₂ O ₃ —3%SiO ₂ (Alumina Fiber)	4.8wt%(5.0wt%)
Total	100wt% (105wt%)
Condition of Interfacial Bubbles	○

[0069] As can be seen from Table 5, bubble formation during glass manufacturing is again suppressed in Example 10 using the paste-form coating material in accordance with the second embodiment of the present invention. The paste of this Example has been found to remain uncrazed even after it is fired and successfully reduce a vaporization loss of platinum, as similar to Examples 1 - 5.

[0070] (EXAMPLES 11 - 13)

These Examples conform to the third embodiment of the present invention.

[Preparation of slurry-form coating material]

A slurry-form coating material was prepared by using OA-10 as a glass component, alumina particles for Al₂O₃ and colloidal silica for SiO₂, as shown in Table 6. The alumina particles and colloidal silica were similar to those used in Example 6. The values written in parentheses in the row of colloidal silica in Table 6 indicate a weight % of a colloidal silica solution. As an organic binder, an aqueous solution containing 1.5 % by weight of a methylcellulose resin was used in the amounts

specified in Table 6 to prepare three types of slurries a1, b1 and c1.

[0071] [TABLE 6]

Slurry	a1	b1	c1
OA-10 (Powder)	50.0wt%	37.5wt%	25.0wt%
Al ₂ O ₃ (Powder)	26.5wt%	39.0wt%	51.5wt%
SiO ₂ (Colloidal Silica)	23.5wt% (94.0wt%)	23.5wt%(94.0wt%)	23.5wt%(94.0wt%)
Organic Binder (1.5 wt.% Aqueous Solution of Methylcellulose Resin)	200wt%	200wt%	200wt%
Total	370.5wt%	370.5wt%	370.5wt%

5 [0072] The glass component (OA-10), Al₂O₃ and SiO₂, were mixed in the ratio specified in Table 7. The mixture was sintered at 1,500 °C for 24 hours to obtain a sintered body. The sintered body was then ground. As a result, ground products a2, b2 and c2 were prepared.

10 [0073] [TABLE 7]

Sintered Body	a2	b2	c2
OA-10 (Powder)	50.0wt%	40.0wt%	37.5wt%
Al ₂ O ₃ (Powder)	26.5wt%	36.5wt%	39.0wt%
SiO ₂ (Powder)	23.5wt%	23.5wt%	23.5wt%
Total	100wt%	100wt%	100wt%
Sintering	1500°C-24 hrs.	1500°C-24 hrs.	1500°C-24 hrs.

[0074] Thereafter, each ground product was mixed with an organic binder and alumina fibers, as shown in Table 8, to prepare three types of pastes a3, b3 and c3.

15 [0075] [TABLE 8]

Paste	a3	b3	c3
Ground Product of Sintered Body	69.7wt% (a2 Sintered Body)	69.7wt% (b2 Sintered Body)	69.7wt% (c2 Sintered Body)
Organic Binder (9 wt. % Aqueous Solution of Methylcellulose Resin)	30.3wt%	30.3wt%	30.3wt%
Alumina Fiber 97%Al ₂ O ₃ -3%SiO ₂	5wt%	5wt%	5wt%
Total	105wt%	105wt%	105wt%

[0076] [Application of coating material to platinum crucible]

While an interior surface of a sand-blasted platinum crucible (46 mm in diameter and 40 mm in height) was heated by a hot air gun, the slurry-form coating material a1, b1 or c1 shown in Table 6 was spray coated on exterior bottom and side surfaces of the platinum crucible and then dried at 80 °C to form a slurry coating material layer.

Next, the paste a3, b3 or c3 shown in Table 8 was adhered onto the thus-formed slurry coating material layer and then dried to form a protective coating material layer.

[0077] Next, the platinum crucible carrying thereon the slurry and protective coating material layers was heated at a heating rate of 10 °C/min to the specified temperature and then maintained at the test temperature for 5 hours, so that such slurry and protective coating material layers were fired. The fired coating film obtained in each Example consisted of a 500 µm thick, fired slurry coating layer and a 5 mm thick, fired protective coating layer.

Each of the platinum crucibles of Examples 11 - 13 on which

the fired coating film was formed in the manner as described above was then cooled to a temperature 200 °C lower than the respective test temperature, filled with an aluminoborosilicate glass (OA-10), heated to the test temperature at a heating rate of 10 °C/min and then maintained at the test temperature for 1 hour. The condition of interfacial bubbles is shown in Table 9.

[0078] [TABLE 9]

	Ex. 11	Ex. 12	Ex. 13
Slurry Coating Layer	a1 (500 μm)	b1 (500 μm)	c3 (500 μm)
Protective Coating Layer	a3 (5mm)	b3 (5mm)	c3 (5mm)
Test Temperature	1200°C	1300°C	1500°C
Condition of Interfacial Bubbles	○	○	○

[0079] As evident from the results shown in Table 9, formation of bubbles during glass manufacturing can be suppressed in Examples 11 - 13 in accordance with the third embodiment of the present invention.

Also, the coating materials of these Examples have been found to successfully reduce a vaporization loss of platinum, as similar to Examples 1 - 5.

[0080] [Exemplary application in glass manufacturing system]

The following examples illustrate a glass manufacturing installation to which the present invention is applied, and a method for manufacturing a display glass by using this apparatus.

First, a construction of the glass manufacturing installation is described. Figure 3 is an explanatory view which shows the construction of the glass manufacturing installation.

The glass manufacturing installation 1 has a generally rectangular melter 2 as a supply source of a molten glass, a refiner 3 disposed downstream of the melter 2, a stir chamber 4 disposed downstream of the refiner 3, and a forming apparatus 5 disposed downstream of the stir chamber 4. The melter 2, refiner 3, stir chamber 4 and forming apparatus 5 are connected by respective connecting flow paths 6, 7 and 8.

[0081] The melter 2 has bottom, side and ceiling walls, each made of a refractory. The melter 2, equipped with a burner, electrodes and others, is capable of melting a raw material for glass. The side wall of the melter 2 that is located toward the downstream has an outlet. This outlet defines an upstream end of the narrow connecting flow path 6 through which the melter 2 is connected to the refiner 3.

[0082] The refiner 3 has bottom, side and ceiling walls. The bottom wall, as well as an interior wall surface (at least an interior wall surface region in contact with a molten glass) of the side wall, are made of platinum or a platinum alloy and surrounded by a protective refractory. A downstream end of the connecting flow path 6 is opened toward the side wall of the refiner 3 that is located toward the upstream. This refiner 3 is a site where fining of a glass is mainly carried out. In

this site, a fining gas released from a fining agent causes fine bubbles included in the glass to inflate and rise so that they are removed from the glass. The side wall of the refiner 3 that is located toward the downstream has an outlet. This outlet defines an upstream end of the narrow connecting flow path 7 through which the refiner 3 is connected to the stir chamber 4 located downstream thereof.

[0083] The stir chamber 4 has bottom, side and ceiling walls. The bottom wall, as well as an interior wall surface (at least an interior wall surface region in contact with a molten glass) of the side wall, are made of platinum or a platinum alloy and surrounded by a protective refractory. The stir chamber 4 is a site where, as a primary task, the molten glass is stirred by a stirrer or the like to homogeneity.

The side wall of the stir chamber 4 that is located toward the downstream has an outlet. This outlet defines an upstream end of the narrow connecting flow path 8 through which the stir chamber 4 is connected to the forming apparatus 5 located downstream thereof.

[0084] The forming apparatus 5, in case it is used to form a display glass, is a sheet glass forming apparatus such as a down-draw, up-draw, or float processing apparatus. An overflow down-draw apparatus is particularly suitable in the formation of a sheet glass for liquid crystal display.

The connecting flow path 6 connecting the melter 2 and

refiner 3 is made of a refractory. On the other hand, the other connecting flow paths, i.e., the connecting flow path 7 connecting the refiner 3 and stir chamber 4 and the connecting flow path 8 connecting the stir chamber 4 and forming apparatus 5, are made of platinum or a platinum alloy and surrounded by a protective refractory.

[0085] In this example, a fired coating film in accordance with the third embodiment of the present invention, which consists of a fired slurry coating layer and the overlying protective coating layer, is formed on an outer surface of the glass manufacturing installation (refiner 3 - connecting flow path 8) made of platinum or a platinum alloy. The coating materials of Examples 11 - 13 can be suitably used for such a fired coating film.

[0086] A display glass can be manufactured using the glass manufacturing installation having the aforesaid construction, according to a method which follows.

First, a raw material for glass is prepared. For example, the glass raw material is prepared such that a glass having a $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-RO}$ (RO denotes at least one of MgO, CaO, BaO, SrO and ZnO) based composition, specifically, an alkali-free glass containing, by mass, 50 - 70 % of SiO_2 , 10 - 25 % of Al_2O_3 , 5 - 20 % of B_2O_3 , 0 - 10 % of MgO, 3 - 15 % of CaO, 0 - 10 % of BaO, 0 - 10 % of SrO, 0 - 10 % of ZnO, 0 - 5 % of TiO_2 and 0 - 5 % of P_2O_5 can be obtained. Besides the above-specified

components, various types of components such as a fining agent can be further added.

[0087] The prepared glass raw material is then introduced in the melter 2 where it is melted and vitrified. Within the melter 2, the glass is heated from above by a burning flame produced by a burner. In case of the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-RO}$ based glass, the glass is melted in the approximate temperature range of 1,500 - 1,650 °C.

After vitrification, the molten glass in the melter 2 is introduced through the connecting flow path 6 into the refiner 3. The molten glass includes initial bubbles produced during a vitrifying reaction. These initial bubbles are removed in the refiner 3 where a fining gas released from a fining agent causes them to enlarge and rise in the glass.

[0088] After being fined in the refiner 3, the molten glass is introduced through the connecting flow path 7 into the stir chamber. In the stir chamber 4, the glass is stirred by a rotating stirrer to homogeneity.

After being homogenized in the stir chamber 4, the molten glass is introduced through the connecting flow path 8 to the forming apparatus 5 where it is formed into a sheet. The display glass is obtained in the manner as described above.

[0089] Generally, the connecting flow path 6 between the melter 2 and the refiner 3 corresponds to the use temperature region of 1,450 - 1,600 °C, the refiner 3, the connecting flow path

7 between the refiner 3 and the stir chamber 4 and the stir chamber
4 to the use temperature region of 1,250 - 1,450 °C, and the
connecting flow path 8 between the stir chamber 4 and the forming
apparatus 5 to the use temperature region of 1,000 - 1,250 °C.

5 In the practice of the above glass manufacturing method,
it has been found that the glass manufacturing installation of
this example shows the reduced platinum vaporization loss, even
after it is operated for an extended period of time, and, as
a result, its strength and stability are maintained over an
10 extended period of time. It has been also found that bubble
formation during glass manufacturing can be suppressed. The
installation of this example is also applicable for use in the
manufacture of glasses other than the display glass, as a matter
of course.

C L A I M S

[1] A coating material for platinum material, which is contemplated to coat a surface of a platinum material made of platinum or a platinum alloy, characterized as containing a refractory component including alumina and silica, and a glass component.

[2] The coating material for platinum material as recited in claim 1, wherein the glass component comprises an alkali-free borosilicate or aluminoborosilicate glass.

[3] The coating material for platinum material as recited in claim 1 or 2, wherein said alumina, silica and glass component are contained in the amounts of 15 - 55 % by weight, 10 - 50 % by weight and 20 - 70 % by weight, respectively.

[4] The coating material for platinum material as recited in any one of claims 1 - 3, wherein said silica is at least partly in the form of colloidal silica.

[5] The coating material for platinum material as recited in claim 4, characterized as containing alumina particles, the glass component and the colloidal silica.

[6] The coating material for platinum material as recited in claim 4, characterized as containing a ground product obtained by grinding a sintered body of a mixture of alumina particles and the glass component, and the colloidal silica.

[7] The coating material for platinum material as recited in

any one of claims 1 - 3, characterized as comprising a slurry containing alumina particles, the glass component and silica particles.

[8] The coating material for platinum material as recited in
5 claim 5, characterized as comprising a slurry containing the alumina particles, the glass component and the colloidal silica.

[9] The coating material for platinum material as recited in claim 6, characterized as comprising a slurry containing the ground product obtained by grinding a sintered body of a mixture
10 of the alumina particles and the glass component, and the colloidal silica.

[10] The coating material for platinum material as recited in any one of claims 7 - 9, characterized in that the slurry contains an organic binder.

15 [11] The coating material for platinum material as recited in any one of claims 1 - 3, characterized as containing a ground product obtained by grinding a sintered body of a mixture of alumina particles, silica particles and the glass component.

[12] The coating material for platinum material as recited in
20 any one of claims 1 - 3, characterized as comprising a paste or green sheet containing alumina particles, silica particles and the glass component.

[13] The coating material for platinum material as recited in claim 11, characterized as comprising a paste or green sheet
25 containing the ground product obtained by grinding a sintered

body of a mixture of the alumina particles, silica particles and glass component.

[14] The coating material for platinum material as recited in claim 12 or 13, characterized in that the alumina particles
5 consist at least partly of fibrous alumina particles.

[15] The coating material for platinum material as recited in any one of claims 12 - 14, characterized in that the paste or green sheet contains an organic binder.

[16] A method for coating a platinum material, characterized
10 in that the coating material as recited in any one of claims 1 - 15 is coated or adhered onto a surface of the platinum material and then fired.

[17] The method for coating a platinum material as recited in claim 16, characterized in that the slurry as recited in any
15 one of claims 7 - 10 is coated on a surface of the platinum material and then fired.

[18] The method for coating a platinum material as recited in claim 17, characterized in that the slurry is spray coated on the surface of the platinum material.

20 [19] The method for coating a platinum material as recited in claim 16, characterized in that the paste or green sheet as recited in any one of claims 12 - 15 is adhered onto the surface of the platinum material and then fired.

[20] The method for coating a platinum material as recited in
25 claim 16, characterized in that the slurry as recited in any

one of claims 7 - 10 is coated on the surface of the platinum material to form a slurry coating layer, the paste or green sheet as recited in any one of claims 12 - 15 is adhered onto the slurry coating layer to form a protective coating layer, and then firing is achieved.

[21] The method for coating a platinum material as recited in any one of claims 16 - 20, characterized in that the surface of the platinum material is subjected to a blasting treatment before the coating material is coated or adhered thereto.

10 [22] A fired coating film for platinum material, which is contemplated to coat a surface of a platinum material made of platinum or a platinum alloy, characterized in that it is obtained by coating or adhering the coating material as recited in any one of claims 1 - 3, 7 and 11 onto the surface of the platinum material and then firing the applied coating material.

15 [23] A fired coating film for platinum material, which is contemplated to coat a platinum material made of platinum or a platinum alloy, characterized in that it includes a matrix phase comprising a glass component and a dispersed phase comprising alumina particles and silica particles and dispersed in the matrix phase.

20 [24] A fired coating film for platinum material, which is contemplated to coat a surface of a platinum material made of platinum or a platinum alloy, characterized in that it is obtained by coating the coating material as recited in any one of claims

4 - 6 and 8 - 10 on the surface of the platinum material and then firing the applied coating material.

[25] A fired coating film for platinum material, which is contemplated to coat a platinum material made of platinum or
5 a platinum alloy, characterized in that it includes a matrix phase comprising a glass component and a colloidal silica component, and a dispersed phase comprising alumina particles and dispersed in the matrix phase.

[26] A fired coating film for platinum material, which is
10 contemplated to coat a surface of a platinum material made of platinum or a platinum alloy, characterized in that it is obtained by adhering the paste or green sheet as recited in any one of claims 12 - 15 onto the surface of the platinum material and then firing the applied paste or green sheet.

15 [27] A fired coating film for platinum material, which is contemplated to coat a surface of a platinum material made of platinum or a platinum alloy, characterized in that it is obtained by coating the slurry as recited in any one of claims 7 - 10 on the surface of the platinum material to form a slurry coating
20 layer, adhering the paste or green sheet as recited in any one of claims 12 - 15 onto the slurry coating layer to form a protective coating layer and then firing the applied coating layers.

[28] The fired coating film for platinum material as recited in claim 27, characterized in that said slurry coating layer
25 includes a matrix phase comprising a glass component and a

colloidal silica component, and a dispersed phase comprising alumina particles and dispersed in the matrix phase.

[29] The fired coating film for platinum material as recited in claim 27 or 28, characterized in that said protective coating
5 layer includes a matrix phase comprising the glass component and a dispersed phase comprising alumina particles and silica particles and dispersed in the matrix phase.

[30] A fired coating film for platinum material, which is contemplated to coat a surface of a platinum material made of
10 platinum or a platinum alloy, characterized in that it is obtained by firing a coating material having a two-layer structure which consists of a first coating layer in contact with the platinum material and comprising a mixture of alumina and silica and a second coating layer provided on the first coating layer and
15 comprising a glass component.

[31] A platinum material made of platinum or a platinum alloy, characterized in that it is coated with the coating material as recited in any one of claims 1 - 15.

[32] A platinum material made of platinum or a platinum alloy,
20 characterized in that it has the fired coating film as recited in any one of claims 22 - 29 on its surface.

[33] A glass manufacturing apparatus using, as a constituent material, a platinum material made of platinum or a platinum alloy, characterized in that its outer surface is coated with
25 the coating material as recited in any one of claims 1 - 15.

[34] A glass manufacturing apparatus using, as a constituent material, a platinum material made of platinum or a platinum alloy, characterized in that its outer surface is covered with the fired coating film as recited in any one of claims 22 - 29.