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(54) **Surface-treated titanium material excellent in oxidation resistance, production method thereof, and engine exhaust system**

(57) Disclosed are a surface-treated titanium material that is excellent in oxidation resistance and allows the excellent oxidation resistance to last for a long period of time and the surface treatment itself to be applied safely at a low cost; the production method thereof; and an exhaust system thereof. A surface-treated titanium material produced by forming an oxidation-resistant baked film, 5 μ m or more in thickness, on a substrate comprising

commercially pure titanium or titanium-base alloy, and said baked film is formed by filling gaps among Al-alloy particles, the baked film comprising Al alloy containing Si by 10 at% or less or commercially pure aluminum with chemical compounds comprising a metallic element M (M represents one or more of Ti, Zr, Cr, Si and Al) and C and/or O.

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Description

[0001] The present invention relates to a surface-treated titanium material that is excellent in oxidation resistance and thus used for a part such as an engine exhaust system requiring oxidation resistance; the production method thereof; and an exhaust system thereof.

[0002] Titanium alloy has a higher specific strength in comparison with a generally used steel material and is increasingly applied to the field of transport vehicles, mostly automobiles, which are intensively directed to weight reduction. In the field, as a material for an exhaust pipe in an exhaust system around an engine, stainless steel is mainly used at present but the application of titanium to an exhaust system has been studied with the aim of weight reduction. The temperature of an exhaust system however rises up to 500°C or higher at some sites. Hence, when a titanium alloy material which is not surface-treated is applied, oxidation progresses fast, the oxidation resistance is inferior at a high temperature, and that causes the problem of durability.

[0003] In this light, in order to improve the high temperature oxidation resistance (hereunder referred to simply as "oxidation resistance") of a titanium material, various surface treatment methods have heretofore been proposed. For example, a material produced by cladding an Al plate on the surface of a titanium alloy is proposed (refer to claims in JP-A No. 99976/1998). Further, a method of applying vapor deposition plating of an Al-Ti type material on the surface of a titanium alloy is proposed (refer to claims in JP-A No. 88208/1994). Furthermore, a method of forming a Ti-Cr-Al-N type film on the surface of a titanium alloy by the PVD method is proposed (refer to claims in JP-A No. 256138/1997).

[0004] However, the problems of those proposals are that the cladding method yields a high cost; and, in the cases of the vapor deposition method and the PVD method, not only the treatment cost is high but also, when a titanium material has a tubular shape like such an exhaust pipe as described above, an oxidation-resistant film can hardly be formed on the inner surface of the pipe.

[0005] To cope with those problems, proposed is a method of depositing an inorganic binder and Al powder on the surface of a titanium alloy, baking them, and thus forming an oxygen barrier film (an oxidation-resistant film) that prevents oxygen from dispersing into the interior of the material; or a treatment method of, after baking them in the above case, applying sealing treatment with a sealer mainly composed of chromic acid in order to fill the gaps formed among Al particles (refer to claims and pages 1 to 3 in JP No. 3151713).

[0006] The oxygen barrier film formed on the surface of a titanium alloy by baking Al powder is effective as an oxidation-resistant film used at a high temperature as mentioned earlier. However, gaps are inevitably formed among the Al particles after baking. As a consequence, it is necessary to fill (seal) the formed gaps with a sealer mainly composed of chromic acid or the like as described in JP No. 3151713 in order to sufficiently exhibit the functions as an oxidation-resistant film.

[0007] To that end, it is necessary to introduce the process of using an inorganic binder to deposit Al powder on a titanium substrate and moreover the process of using chromic acid to fill the gaps formed among Al particles after baking, namely two-step treatment is required, and thus it is not efficient. Further, the chromic acid solution only described as the inorganic binder is extremely poisonous and hence the safety of not only the treatment processes but also the usage as a member is concerned.

[0008] The present invention has been established in view of the above situation and the object thereof is to provide a surface-treated titanium material that is excellent in oxidation resistance and allows the excellent oxidation resistance to last for a long period of time and the surface treatment itself to be applied safely at a low cost; the production method thereof; and an exhaust system thereof.

[0009] The gist of a surface-treated titanium material excellent in oxidation resistance according to the present invention aimed at attaining the above object is that the surface-treated titanium material is produced by forming an oxidation-resistant baked film 5 μm or more in thickness on a substrate comprising commercially pure titanium or titanium-base alloy; and the baked film is formed by filling the gaps among particles comprising Al alloy containing Si by 10 at% or less or commercially pure aluminum with chemical compounds comprising a metallic element M (M represents one or more of Ti, Zr, Cr, Si and Al) and C and/or O.

[0010] Further, the gist of a method of producing a surface-treated titanium material excellent in oxidation resistance according to the present invention aimed at attaining the above object is that an oxidation-resistant film is formed on a substrate comprising titanium or titanium-base alloy by coating the substrate with a solution containing Al alloy particles containing Si by 10 at% or less or commercially pure aluminum particles and organometallic compounds comprising a metallic element M (M represents one or more of Ti, Zr, Cr, Si and Al) and C and/or O; and baking them.

[0011] Furthermore, the gist of an engine exhaust system excellent in oxidation resistance according to the present invention aimed at attaining the above object is that the exhaust system is made of the surface-treated titanium material.

[0012] As explained above, an oxygen barrier film formed on the surface of a titanium alloy by baking Al powder is effective as an oxidation-resistant film at a high temperature. However, also as explained above, since gaps are inevitably formed among the Al particles after baking, it is necessary to fill (seal) the formed gaps with a sealer or the like in order to sufficiently exhibit the functions as an oxidation-resistant film.

[0013] For that purpose, the present invention uses, as a sealer, a substance which, after baking, forms chemical compounds comprising a metallic element M (M represents one or more of Ti, Zr, Cr, Si and Al) and C and/or O. When the chemical compounds comprising the metallic element M and C and/or O exist among the heretofore known particles of commercially pure aluminum type or Al-Si alloy containing Si by 10 at% or less in the baked film, the high temperature oxidation resistance of the baked film improves remarkably.

[0014] In addition, the chemical compounds comprising a metallic element M and C and/or O also play the role of the binder of Al powder and thus improve the adhesiveness among Al particles in the baked film or between the baked film and the surface of a titanium material. Here, the coating of the surface of a titanium material with organometallic compounds comprising a metallic element M (M represents one or more of Ti, Zr, Cr, Si and Al) and C and/or O as the raw materials of the chemical compounds can be applied at the same time as the coating thereof with Al powder and is simple and easy to apply as indicated in the gist of the production method of a surface-treated titanium material according to the present invention. Furthermore, the chemical compounds are not poisonous unlike the chromic acid that has heretofore been used and assure safety not only in the surface treatment process but also in the application to a member.

[0015] The embodiments of the present invention and the reasons for limiting the requirements stipulated in the present invention are concretely explained hereunder.

(Al powder)

[0016] Commercially pure aluminum powder or Al-Si alloy powder containing Si by 10 at% or less according to the present invention is a basic component to improve the oxidation resistance of a baked film on the surface of a titanium material. The Al powder used may be any of commercially pure aluminum (commercially pure aluminum type powder), Al-Si alloy powder containing Si by 10 at% or less, and a mixture thereof, and the Al-Si alloy powder may be a mixture of Al powder and Si powder.

[0017] In the case of Al-Si alloy powder, since it contains Si, the oxidation resistance at a higher temperature improves. However, the effect of an Si content is saturated with the content of about 10 at% and moreover, when Si is contained 10 at% or more, the powder itself is hardly produced. For that reason, an Si content is set at 10 at% or less.

[0018] Such Al powder can be produced by any of the known methods such as the molten metal direct powdering method including the atomization method, the molten metal agitation method and the rotating disc dripping method; and the mechanical powdering method including the stamp mill method, the ball mill method, the vibration mill method and the attriter method. By any of the powder producing methods, Al powder having an average particle diameter in the range from about 2 to 500 μm is produced.

[0019] Note that, when the particle diameter of such Al powder is too large, many gaps are formed undesirably among the particles though it also depends on the thickness of a baked film. In this light, in order to inhibit to the utmost the gaps from forming among the particles as stated above, it is desirable to regulate the average particle diameter of Al powder to be coated to 20 μm or smaller and to select and use Al powder 20 μm or smaller in average particle diameter.

(Sealer)

[0020] Chemical compounds, as a sealer, comprising a metallic element M (M represents one or more of Ti, Zr, Cr, Si and Al) and C and/or O play the role of filling the gaps among Al powder particles and improving the oxidation resistance of a baked film in the present invention. Further, the chemical compounds also play the role of a binder of Al powder and improving the adhesiveness among Al particles in a baked film or between the baked film and the surface of a titanium material.

[0021] In order to form chemical compounds comprising a metallic element M (M represents one or more of Ti, Zr, Cr, Si and Al) and C and/or O among Al particles in a baked film, organometallic compounds comprising a metallic element M (M represents one or more of Ti, Zr, Cr, Si and Al) and C and/or O are applied on the surface of a titanium material before baking.

[0022] As such organometallic compounds, it is preferable to use the organometallic compounds such as acetylacetone titanium solution, acetylacetone zirconium solution, chromium acetate, silicone, silica sol, alumina sol, and aluminum isopropoxide. The reason is that such organometallic compounds are stable, easy to handle, and less toxic.

[0023] As the metallic element M, Si is preferably used in particular from the viewpoint of the improvement of the oxidation resistance of a baked film at a high temperature. Hence, a particularly preferable metallic element M is the one which inevitably contains Si though it may also contain other metallic elements. For example, when a silicone resin is selected as an organometallic compound comprising Si and C and/or O and a solution containing Al powder and the silicone resin is applied on the surface of a titanium material and baked, chemical compounds comprising Si-O-C are formed among the Al particles and play the role of a sealer. In addition, the chemical compounds act as an excellent binder.

[0024] Usually the ratio Si/O in a silicone resin is around one but, by selecting an appropriate baking temperature, the reaction between O and Si is accelerated and the ratio Si/O lowers. Thereby chemical compounds among particles are

more stabilized and high oxidation resistance can be obtained. The reason is presumably that the chemical compounds come close to SiO_2 which is the most stable oxide by selecting a baking temperature appropriately. In order to do so, a preferable baking temperature is in the range from 200°C to 400°C. However, since a binder portion hardens by the baking and cracking is likely to occur, when working such as bending is applied, it is recommended to apply baking after working such as bending. The amount of Si-O chemical bond can be controlled by changing a baking temperature in an appropriate manner.

[0025] In addition to Si as a metallic element M or a silicone resin as an organometallic compound, the aforementioned organometallic compounds such as acetylacetone titanium solution, acetylacetone zirconium solution, chromium acetate, silica sol, alumina sol, and aluminum isopropoxide can form the most stable oxides such as TiO_2 , ZrO_2 , Al_2O_3 , Cr_2O_3 and the like even after baked at a high temperature and exhibit high oxidation resistance. In addition, the chemical compounds act as an excellent binder.

[0026] In any of those cases, there exists the chemical bond M-O of a metallic element M and oxygen, such as Si-O-C in the case of using Si, Ti-O in the case of using Ti, Zr-O in the case of using Zr, Cr-O in the case of using Cr, and Al-O in the case of using Al, as the metallic element M, in the baked film. In this way, when a chemical bond M-O of a metallic element M and oxygen exists in a baked film, the oxidation resistance of the baked film at a high temperature particularly improves. In this case, it is preferable that the ratio M/O is in the range from 0.4 to 2.

(Baked film)

[0027] It is preferable that the chemical compounds comprising a metallic element M and C and/or O are contained by 5 to 50 vol% in a baked film in order to serve as both a binder and a sealer. For example, even when spherical Al particles of an identical size are ideally filled, about 26% in volume percentage of the baked film is space and the space must be filled. In other words, when the chemical compounds are in the closest packed state, the volume percentage of the chemical compounds in the baked film is 26%. In contrast, when Al particles of different sizes are mixed, the volume percentage of the space in a baked film is even larger and the packing factor of chemical compounds increases. Hence the volume percentage of the chemical compounds in a baked film is set at about 5 to 50 vol%.

(Baked film thickness)

[0028] The thickness of a baked film is set at 5 μm or more. The thickness of less than 5 μm is too thin to exhibit the oxygen barrier effect of the baked film itself. On the other hand, even when the thickness exceeds 200 μm , the oxygen barrier effect is saturated and hence a preferable upper limit of the thickness is set at 200 μm .

[0029] The ratio Al/Si in a baked film in the case of using a silicone resin or the like can be measured by an ordinary surface element analyzing method such as EDX or the like. Further, with regard to the method of identifying the existence of the chemical compounds comprising M and C-O among Al particles in a baked film, the existence of the relevant elements can be identified by the elemental analysis on a section (a cut surface or a fractured surface) of a baked film. Furthermore, the bonds of M-O and M-C in a baked film can be detected by XPS. The chemical bond M-O between a metallic element M and O, for example Si-O, can be analyzed by XPS or FTIR.

(Titanium oxide layer)

[0030] By oxidizing the surface of a substrate comprising commercially pure titanium or titanium-base alloy and forming an oxide film before a baked film is formed, it becomes possible to improve the adhesiveness between the baked film and the substrate and thus to obtain higher oxidation resistance. In this case, the surface-treated titanium material has a titanium oxide layer between the baked film and the substrate.

[0031] The adhesiveness of a sealer (chemical compounds comprising a metallic element M and C and/or O) on the surface of Al particles with the surface of a substrate may be insufficient in some uses. In such a case, according to JP No. 3151713 mentioned earlier or others, surface coarsening treatment such as shot blasting is applied and the adhesiveness is improved by the anchor effect. However, the surface coarsening treatment may not be applied to a substrate in some uses. In such a case, when oxidation treatment is applied and a titanium oxide film is formed on the surface of a substrate beforehand, the adhesiveness of the sealer with the formed titanium oxide film improves remarkably.

[0032] The oxidation treatment may be applied by heating in the air (a recommended temperature is in the range from 300°C to 500°C) or by a wet process such as anodizing. The effect of the oxide layer almost does not change as long as the thickness thereof is in the range from 0.1 to 5 μm . Here, a oxide layer can be observed and the thickness thereof can be measured on a section by SEM or, when the thickness is thin, by TEM.

(Hot-dip aluminum plated layer)

[0033] It is possible to further improve the corrosion resistance of a substrate by forming a hot-dip aluminum plated layer on the surface of the substrate comprising commercially pure titanium or titanium-base alloy before a baked film is formed. In this case, the surface-treated titanium material has the hot-dip aluminum plated layer between the baked film and the substrate. The hot-dip aluminum plated layer itself has oxidation resistance and, by overlaying a baked film of the present invention thereon, the corrosion resistance of the substrate can further be improved and moreover the appearance of the hot-dip aluminum plated layer is also improved.

(Production method of surface-treated titanium material)

[0034] A method of producing a surface-treated titanium material according to the present invention, as stated earlier, is that an oxidation-resistant film is formed on a substrate comprising titanium or titanium-base alloy by coating the substrate with a solution containing Al alloy particles containing Si by 10 at% or less or commercially pure aluminum particles and organometallic compounds comprising a metallic element M (M represents one or more of Ti, Zr, Cr, Si and Al) and C and/or O; and baking them.

(Coating solution)

[0035] In the above case, as a solution applied on the surface of a substrate, any kind of an aqueous solution or a solvent may be used as long as the solution can uniformly disperse and dissolve relevant chemical compounds. Further, with regard to a solid matter ratio of metallic particles (Al, Si, and/or a metallic element M) to C and/or O in a coating solution, it is preferable that the metallic particles are contained at least by 5 wt% of C and/or O chemical compounds. When the content of metallic particles is less than 5 wt%, there is the fear that the metallic particles (Al, Si, and/or a metallic element M) in a baked film are insufficient and the oxidation resistance and adhesiveness may not sufficiently be secured. In contrast, when the metallic particles are contained in excess of 80 wt% of C and/or O chemical compounds inversely, the film that retains particles is hardly formed and thus the problems of the adhesiveness and durability of the baked film may rather arise. For those reasons, a preferable solid matter ratio of metallic particles to C and/or O in a coating solution is in the range from 5 to 80 wt%.

(Baking)

[0036] In the baking process, the organometallic compounds applied as above is oxidized, a baked film filled with chemical compounds comprising a metallic element M (M represents one or more of Ti, Zr, Cr, Si and Al) and C and/or O is formed among Al particles, and thus the oxidation resistance, adhesiveness, and durability of the baked film are improved.

[0037] With regard to a baking temperature for this purpose, an appropriate temperature is selected in accordance with the applied organometallic compounds or the conditions of other coating materials. That is, as exemplified earlier in the case of a silicone resin, a baking temperature that allows baked chemical compounds to obtain the amount of the chemical bond M-O enough to exhibit high oxidation resistance is properly selected. Though a baking temperature has been in the range from 200°C to 400°C in the case of a silicone resin, in the case of baking one or more kinds of organometallic compounds selected from among acetylacetone titanium solution, acetylacetone zirconium solution, chromium acetate, silica sol, alumina sol, and aluminum isopropoxide, a preferable baking temperature is in the range from 200°C to 500°C. Here, the baking time is defined by the time required for exhibiting the aforementioned effect of baking at a selected temperature.

[0038] Further, with regard to a baking atmosphere, in the same way as an ordinary baking atmosphere, any atmosphere can be employed as long as it is an oxidizing atmosphere and the air, an oxygen contained atmosphere or the like is properly selected.

(Post-treatment)

[0039] When higher oxidation resistance is required after such an oxidation-resistant baked film is formed, it is possible to apply post-treatment after the baked film has been formed and thus to eliminate the gaps, among Al particles, slightly remaining on the surface of the baked film. As the post-treatment, blasting treatment using hard particles, such as shot blasting, is preferably employed, and, by the blasting treatment, it is possible to impose impact on the surface of the baked film and to eliminate the gaps, among Al particles, slightly remaining.

[0040] Further, when such blasting treatment is applied, it is also possible to obtain a beautiful surface of metallic luster by removing only the surface layer of the Al oxide film formed on the surface at the time of baking or the chemical

compounds comprising a metallic element M (M represents one or more of Ti, Zr, Cr, Si and Al) and C and/or O.

(Titanium material used)

[0041] A titanium substrate cited in the present invention means a titanium material comprising commercially pure titanium or titanium-base alloy formed into various shapes by plastic working such as rolling. The present invention does not stipulate a titanium material to be subjected to surface treatment but any of α alloy, α - β alloy and β alloy may be adopted in accordance with the properties (mechanical properties and others) required for the use. For example, commercially pure titanium (JIS class 2), Ti-1.5Al, Ti-0.5Al-0.45Si-0.2Nb, Ti-6Al-4V, Ti-3Al-2.5V, Ti-15V-3Al-3Sn-3Cr and others can be used.

[0042] Further, when used for an exhaust system in particular, it is preferable to use the titanium alloy disclosed in JP-B No. 071275/2004 applied earlier by the present inventors. More specifically, it is desirable to use a titanium alloy material: containing Al of 0.30 to 1.5% and Si of 0.10 to 1.0% in mass; more desirably having the ratio Si/Al of 1/3 in mass; or yet more desirably selectively containing Nb of 0.1 to 0.5%. An Al content is set at 0.30% or more in order to improve heat resistance and high temperature oxidation resistance and 1.5% or less in order to preventing ductility and corrosion resistance from deteriorating. Si, by combined addition with Al, improves high temperature strength and also improves high temperature oxidation resistance, in particular resistance to scale loss and resistance to the formation of an oxygen diffusion layer, while suppressing the deterioration of corrosion resistance to the minimum. Further, Si improves fatigue properties and brittleness by suppressing crystal grain growth. An Si content is set at 0.10% or more in order to obtain the effects and 1.0% or less in order to prevent formability and corrosion resistance from deteriorating. Furthermore, by selectively containing Nb by 0.1% or more, it is possible to improve high temperature oxidation resistance, in particular resistance to scale loss and resistance to the formation of an oxygen diffusion layer, while suppressing the deterioration of corrosion resistance to the minimum. Meanwhile, an Nb content is set at 0.5% or less in order to prevent formability from deteriorating.

EXAMPLE

[0043] Next, the present invention is explained more concretely on the basis of examples. However, the present invention is, in the nature of things, not limited by the after-mentioned examples but can be applied by appropriately modifying them within the range conforming to the aforementioned and after-mentioned tenor of the present invention and all the modifications are included in the technological scope of the present invention.

Example 1

[0044] Oxidation-resistant baked films containing chemical compounds (chemical compounds comprising a metallic element M and C and/or O) of various Si/O ratios among Al particles as shown in Table 1 were formed on the surfaces of titanium substrates by applying solutions containing the mixture of Al powder and silicone on the surfaces under the coating conditions shown in Table 1; and baking them. Those samples were subjected to high temperature oxidation tests and the oxidation resistance was evaluated by the weight gain after the oxidation tests. The results of the evaluation are shown in Table 1.

[0045] As titanium substrates, commercially pure titanium rolled sheets (JIS class 3, 1 mm in thickness) were used. The coating solutions were produced by mixing commercially pure aluminum particles 5 μ m in average particle diameter (described as Al in the table) or Al alloy particles of various Si contents (described as Al-Si in the table) and silicone into an organic solvent comprising ethanol or isopropanol.

[0046] Coating was applied by dipping and, in every case, an oxidation-resistant film about 30 μ m in thickness was formed by drying it for 0.5 hour at 120°C and thereafter baking it for 0.5 hour at 250°C.

[0047] Further, in order to clarify the influence of titanium oxide layers (preparatory oxide layers) on surfaces, the aforementioned oxidation-resistant baked films were formed also on the titanium substrates being oxidized in the temperature range from 500°C to 700°C beforehand and having the oxide layers of various thicknesses (Nos. 9 to 12 in Table 1). The thicknesses of the oxide layers are also shown in Table 1.

[0048] In the high temperature oxidation tests, the weight gain of a sample was measured after the sample was exposed for 100 hours at 800°C in a high temperature atmospheric air and thereby high temperature oxidation resistance was evaluated.

[0049] In the invention examples Nos. 3 to 12 (note that Nos. 7 and 8 were reference examples) in Table 1, the weight gain after subjected to oxidation test was about 2.5 mg/cm² at the highest. In contrast, in the comparative example No. 1, the substrate itself was not subjected to surface treatment and the oxidation-resistant baked film itself was not formed. Thereby the weight gain after the high temperature oxidation test was as high as 12 mg/cm². Further, in the comparative example No. 2, the oxidation-resistant baked film was composed of only Al particles and chemical compounds (chemical

compounds comprising a metallic M and C and/or O) were not formed among Al particles. Thereby the weight gain after the high temperature oxidation test was as high as 8.9 mg/cm². In conclusion, it is understood that the high temperature oxidation resistance in the invention examples Nos. 3 to 12 was remarkably more excellent than that in the comparative examples Nos. 1 and 2.

[0050] In addition, the high temperature oxidation resistance in the invention examples Nos. 9 to 12 wherein titanium oxide layers (preparatory oxide layers) were formed on the substrates was generally more excellent than that in the invention examples Nos. 3 to 8 wherein no titanium oxide layers were formed.

[0051] Here, in the cases of the reference examples Nos. 7 and 8, though the high temperature oxidation resistance was excellent, the Si contents in Al exceeded 10 at%. Hence, the production of the Al powder itself was difficult and inappropriate industrially, and therefore the cases were regarded as reference examples.

Table 1

Category	No.	Coating conditions of titanium material				Baked film		
		Al powder used		Titanium oxide layer (μm)	Organometallic compound	Chemical compound among Al particles	Si/O ratio	Weight gain by oxidation mg/cm ²
		Type	Si amount (at%)					
Comparative example	1	Nil	0	Nil	Nil	Nil	Nil	12
Comparative example	2	Al	0	Nil	Nil	Nil	Nil	8.9
Invention example	3	Al	0	Nil	Silicone	Si-C-O	0.46	2.5
Invention example	4	Al-Si	2	Nil	Silicone	Si-C-O	0.51	1.6
Invention example	5	Al-Si	5	Nil	Silicone	Si-C-O	0.48	1.5
Invention example	6	Al-Si	8	Nil	Silicone	Si-C-O	0.45	1.3
Invention example	7	Al-Si	13	Nil	Silicone	Si-C-O	0.48	1.5
Invention example	8	Al-Si	20	Nil	Silicone	Si-C-O	0.45	1.6
Invention example	9	Al	0	0.3	Silicone	Si-C-O	0.46	2.5
Invention example	10	Al	0	0.7	Silicone	Si-C-O	0.47	1.1
Invention example	11	Al	0	1	Silicone	Si-C-O	0.48	0.9
Invention example	12	Al	0	3	Silicone	Si-C-O	0.49	1

Example 2

[0052] Oxidation-resistant baked films containing chemical compounds (chemical compounds comprising a metallic element M and C and/or O) among Al particles as shown in Table 2 were formed on the surfaces of titanium substrates by applying solutions containing the mixture of Al powder and various organometallic compounds (the chemical formulae are also shown in Table 2 except silicone) on the surfaces under the coating conditions shown in Table 2; and baking them, under the same conditions as Example 1. Those samples were subjected to high temperature oxidation tests and the oxidation resistance was evaluated by the weight gain after the oxidation tests in the same way as Example 1. The results of the evaluation are shown in Table 2.

[0053] The concrete conditions of titanium substrates, coating solutions, Al particles, coating and baking, high temperature oxidation tests were the same conditions as employed in Example 1 except the kinds of organometallic compounds.

[0054] In the invention examples Nos. 13 to 18 shown in Table 2, the weight gain after the oxidation test was about 2.4 mg/cm² at the highest even in the cases of using organometallic compounds other than silicone. Here, the high temperature oxidation resistance in the invention examples Nos. 13 and 18 wherein silicone was used was comparatively more excellent than that in the invention examples Nos. 14 to 17 wherein organometallic compounds other than silicone were used. From this fact, it is understood that Si was particularly desirable as the metallic element M from the viewpoint of improving the high temperature oxidation resistance of a baked film.

[0055] The results of the comparative examples Nos. 1 and 2 were the same as those of the comparative examples Nos. 1 and 2 of Example 1 (Table 1). In conclusion, it is understood that the high temperature oxidation resistance in the invention examples Nos. 13 to 18 was remarkably more excellent than that in the comparative examples Nos. 1 and 2.

Table 2

Category	No.	Coating conditions of titanium material			Baked film	
		Al powder used		Organometallic compound	Chemical compound among Al particles	Weight gain by oxidation mg/cm ²
		Type	Si amount (at%)			
Comparative example	1	Nil	0	Nil	Nil	12
Comparative example	2	Al	0	Nil	Nil	8.9
Invention example	13	Al	0	Silicone	Si-C-O	1
Invention example	14	Al	0	Chromium acetate Cr(CH ₃ COO) ₂	Cr-C-O	2.1
Invention example	15	Al	0	Aluminum isopropoxide Al[OCH(CH ₃) ₂] ₃	Al-C-O	1.2
Invention example	16	Al	0	Acetylacetone titanium solution Ti(OC ₄ H ₉) ₂ (C ₅ H ₇ O) ₂	Ti-C-O	2.2
Invention example	17	Al-Si	5	Acetylacetone zirconium solution Zr(OC ₄ H ₉) ₂ (C ₅ H ₇ O) ₂	Zr-C-O	2.4
Invention example	18	Al-Si	7	Silicone	Si-C-O	1.1

Example 3

[0056] Surface treatment according to the present invention was applied to the aforementioned desirable titanium alloy materials, as the titanium substrates, containing, in mass, Al of 1.0%, Si of 0.33%, namely the ratio Si/Al being 1/3 in mass, and selectively Nb of 0.2%. That is, oxidation-resistant baked films containing chemical compounds (chemical compounds comprising a metallic element M and C and/or O) among Al particles as shown in Table 3 were formed on the surfaces of the titanium alloy materials by applying solutions containing the mixture of Al powder and silicone on the surfaces under the coating conditions shown in Table 3; and baking them, under the same conditions as Example 1. Those samples were subjected to high temperature oxidation tests and the oxidation resistance was evaluated by the weight gain after the oxidation tests in the same way as Example 1. The results of the evaluation are shown in Table 3.

[0057] Here, hot-dip aluminum plated layers with the thicknesses shown in Table 3 were formed on the titanium substrates beforehand. The titanium alloy materials not containing Nb were used as the titanium substrates of the invention examples Nos. 19 and 21 shown in Table 3 and the titanium alloy materials containing Nb were used as the titanium substrates of the invention examples Nos. 20, 22 and 23 shown in Table 3.

[0058] Further, in the cases of the titanium substrates used in the invention examples Nos. 20 and 22 shown in Table 3, the formed baked films were subjected to blast treatment (gas pressure of 3 kg/cm²) of alumina-made hard particles (50 μm in average particle diameter) for 10 seconds through a commercially available shot blasting machine.

[0059] The concrete conditions of titanium substrates, coating solutions, Al particles, coating and baking, high temperature oxidation tests were the same conditions as employed in Example 1.

[0060] As seen in Table 3, the high temperature oxidation resistance of the surface-treated titanium materials, of the invention examples Nos. 20 to 23, prepared by forming hot-dip aluminum plated layers on the titanium substrates beforehand was remarkably more excellent than that of the comparative examples Nos. 1 and 2 which were the same as Example 1. Further, as seen in Table 3, the high temperature oxidation resistance in the invention examples Nos. 20, 22 and 23 wherein hot-dip aluminum plated layers or even thicker hot-dip aluminum plated layers were formed was more excellent than that in the invention example No. 19 wherein a hot-dip aluminum plated layer was not formed and the invention example No. 21 wherein a rather thinner hot-dip aluminum plated layer was formed. The shot blasting treatment also contributed to the improvement of the high temperature oxidation resistance in the invention examples Nos. 20 and 22.

[0061] Those results from the examples support the significance of the critical requirements and preferable requirements of the present invention concerning the improvement of the high temperature oxidation resistance of a titanium material. Further, from those results, it is understood that the present invention makes it possible to obtain a surface-treated titanium material that is excellent in oxidation resistance and allows the excellent oxidation resistance to last for a long period of time and the surface treatment itself to be applied safely at a low cost.

Table 3

Category	No.	Coating conditions of titanium material				Baked film	
		Al powder used		Hot-dip aluminum plated layer (μm)	Organometallic compound	Chemical compound among Al particles	Weight gain by oxidation mg/cm ²
		Type	Si amount (at%)				
Comparative example	1	Nil	0	Nil	Nil	Nil	12
Comparative example	2	Al	0	Nil	Nil	Nil	8.9
Invention example	19	Al	0	Nil	Silicone	Si-C-O	1.7
Invention example	20	Al	0	20	Silicone	Si-C-O	0.9
Invention example	21	Al-Si	10	1	Silicone	Si-C-O	1.8
Invention example	22	Al-Si	10	5	Silicone	Si-C-O	1.1
Invention example	23	Al-Si	10	15	Silicone	Si-C-O	0.7

[0062] The present invention makes it possible to provide a surface-treated titanium material that is excellent in oxidation resistance and allows the excellent oxidation resistance to last for a long period of time and the surface treatment itself to be applied safely at a low cost; the production method thereof; and an engine exhaust system thereof.

Claims

1. A surface-treated titanium material excellent in oxidation resistance, wherein said surface-treated titanium material is produced by forming an oxidation-resistant baked film 5 μm or more in thickness on a substrate comprising commercially pure titanium or titanium-base alloy; and said baked film is formed by filling the gaps among particles comprising Al alloy containing Si by 10 at% or less or commercially pure aluminum with chemical compounds comprising a metallic element M (M represents one or more of Ti, Zr, Cr, Si and Al) and C and/or O.
2. The surface-treated titanium material according to claim 1, wherein said particles comprise Al alloy containing Si by 2 to 10 at%.
3. The surface-treated titanium material according to claim 1 or 2, wherein said metallic element M contains Si.
4. The surface-treated titanium material according to claim 3, wherein the chemical bond of Si and O exists in said

baked film and the ratio Si/O satisfies the expression $0.4 \leq \text{Si/O} \leq 2$.

- 5 5. The surface-treated titanium material according to any one of claims 1 to 4, wherein a titanium oxide layer is formed between said baked film and said substrate.
6. The surface-treated titanium material according to any one of claims 1 to 5, wherein a hot-dip aluminum-plated layer is formed on said substrate beforehand and said oxidation-resistant baked film is formed on said hot-dip aluminum-plated layer.
- 10 7. The surface-treated titanium material according to any one of claims 1 to 6, wherein said chemical compounds comprising said metallic element M and C and/or O are formed by baking one or more kinds of organometallic compounds selected from among acetylacetone titanium solution, acetylacetone zirconium solution, chromium acetate, silicone, silica sol, alumina sol, and aluminum isopropoxide.
- 15 8. A method of producing a surface-treated titanium material excellent in oxidation resistance, wherein an oxidation-resistant film is formed on a substrate comprising titanium or titanium-base alloy by coating said substrate with a solution containing Al alloy particles containing Si by 10 at% or less or commercially pure aluminum particles and organometallic compounds comprising a metallic element M (M represents one or more of Ti, Zr, Cr, Si and Al) and C and/or O; and baking them.
- 20 9. The method of producing a surface-treated titanium material according to claim 8, **characterized by** applying blasting treatment with hard particles to said baked film.
- 25 10. An engine exhaust system made of said surface-treated titanium material according to any one of claims 1 to 7.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 05 01 3365

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