



US 20070026249A1

(19) **United States**

(12) **Patent Application Publication** (10) **Pub. No.: US 2007/0026249 A1**

Strietzel (43) **Pub. Date: Feb. 1, 2007**

(54) **VENEERABLE SILVER ALLOY FOR PRODUCING CERAMIC-VENEERED DENTAL RESTORATIONS**

(52) **U.S. Cl.** **428/469; 420/580**

(57) **ABSTRACT**

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An alloy that can be fired onto, for producing ceramic-faced dental restorations, comprising or consisting of:

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(21) Appl. No.: **11/495,992**

(22) Filed: **Jul. 28, 2006**

(30) **Foreign Application Priority Data**

Jul. 29, 2005 (EP) 05 107 053.0

Publication Classification

(51) **Int. Cl.**
C22C 30/00 (2006.01)

Silver	40-45 wt. %,
Gold	37.5-45 wt. %,
Palladium	0-14.5 wt. %,
Indium, zinc, tin, copper, lanthanoids, scandium, lanthanum	in total 5.5-15 wt. %,
Manganese	0.1-5 wt. %,
Tantalum, platinum, iridium, osmium, ruthenium, rhodium, rhenium, titanium, niobium, zirconium, tungsten, vanadium	in total 0.05-5 wt. %,
Gallium, iron	0-5 wt. %,
Other metals, semimetals and impurities	0-1 wt. %,

is described, wherein the data relating to percentage by weight are each with respect to the total weight of the alloy.

VENEERABLE SILVER ALLOY FOR PRODUCING CERAMIC-VENEERED DENTAL RESTORATIONS

[0001] This application claims priority from European Patent Application 05107053.0, filed Jul. 29, 2005, the full disclosure of which is hereby incorporated by reference herein.

[0002] The invention provides an alloy that can be fired onto, for producing dental restorations that can be veneered with ceramic, for example for producing crowns, bridges, superstructures and other tooth prostheses that are intended to be provided with a ceramic surface but also for non-faced restorations such as inlays, onlays, auxiliary parts, etc.

[0003] The escalation of costs in the public health service is also leading to intense pressure on the cost of materials. In the field of dentistry, noble metal (NM) alloys are used as well as noble metal-free alloys. They are used in particular for inlays and onlays as well as crown and bridge frameworks. The latter structures may be faced entirely or partly with ceramic or a plastic material. Due to the high cost of the raw material for NM alloys (e.g. gold, platinum), this group of alloys is unacceptably expensive for a large section of the population. Thus there is a constant search for cost-effective NM alloys. In this connection, the use of silver alloys is frequently a suitable alternative.

[0004] Silver-containing NM alloys have been disclosed in particular in the following documents:

[0005] WO 03/028669 A1, EP 1 346 718 A1, EP 1 340 482 A1, EP 0 973 480 B1, NL 9200566, U.S. Pat. No. 6,290,501 B1, U.S. Pat. No. 3,929,474, U.S. Pat. No. 4,008,080, DE 100 33 445 A1, U.S. Pat. No. 5,453,290, EP 475 528 B2.

[0006] A number of alloys based on silver, which can be fired onto (veneerable alloys), are also commercially available. In most cases these are silver-palladium alloys, i.e. the second most abundant constituent in the alloy is generally palladium. In many cases gold is the second most abundant constituent in the alloy.

[0007] In practice, silver alloys that can be fired onto (veneerable silver alloys), are frequently veneered with ceramics, the linear coefficient of thermal expansion (CTE) of which is in the range of about 15-18 [10^{-6} K^{-1}] over the range 25 to 500° C. The alloy that can be fired onto, according to the invention is also intended to be faced (veneered) with this kind of veneering ceramic.

[0008] When designing new alloys based on silver-gold that can be fired onto, a person skilled in the art has to take into account a number of technical properties and attempt to adjust selected properties in a particularly beneficial way without thereby having a particularly disadvantageous effect on the other properties.

[0009] In addition to the mechanical properties, chemical and biological factors also have to be considered. Included among the mechanical properties are:

[0010] Mechanical strength (modulus of elasticity, 0.2% offset yield strength, tensile strength, elongation limit)

[0011] Heat resistance

[0012] Coefficient of thermal expansion (CTE)

[0013] Hardness

[0014] Included among the chemical properties to be considered are corrosion and discoloration. The latter in particular can cause problems. Silver tends to react e.g. with

sulfides and other sulfur-containing groups. The reaction product, silver sulfide, is black and has a permanent and deleterious effect on the aesthetic appearance.

[0015] The biological properties (toxic or allergic reactions) depend mainly on the corrosion characteristics. Therefore the release of ions must be kept as low as possible. But the type of ions released also has to be considered. Thus, copper and silver ions act as bactericides, and this is evaluated as basically positive. However, in increasing concentration, these elements are cytotoxic and that can cause localised toxic reactions.

[0016] In view of the problems described above when using traditional silver alloys, the object underlying the present invention was to provide a silver alloy (i) the casting point of which is clearly recognisable, (ii) that has a particularly good fit after casting (high fitting accuracy of the frameworks cast from the alloy) (dental restorations), in particular in the case of large spans), (iii) that can be veneered with conventional veneering ceramics with a CTE in the range 15-17 [10^{-6} K^{-1}], (iv) have a high resistance to corrosion and (v) are biocompatible. Further objects underlying the present invention can be obtained from the description that follows and the accompanying claims.

[0017] In the case of the silver alloy identified, the other alloy features and alloy properties that are important for a dental alloy that can be fired onto, should lie within the ranges preferred by a person skilled in the art.

[0018] According to the invention, the object underlying the invention is achieved by an alloy that can be fired onto, for producing ceramic-faced dental restorations, comprising or consisting of:

Silver	40-45 wt. %,
Gold	37.5-45 wt. %,
Palladium	0-14.5 wt. %,
Indium, zinc, tin, copper, lanthanides, scandium, lanthanum	in total 5.5-15 wt. %,
Manganese	0.1-5 wt. %,
Tantalum, platinum, iridium, osmium, ruthenium, rhodium, rhenium, titanium, niobium, zirconium, tungsten, vanadium	in total 0.05-5 wt. %,
Gallium, iron	0-5 wt. %,
Other metals, semimetals and impurities	0-1 wt. %,

wherein the data relating to percentage by weight are each with respect to the total weight of the alloy.

[0019] The alloy that can be fired onto according to the invention contains a proportion of 40-45 wt. % of silver. As a result of the high silver content, a more favourable price for the material can be achieved than for a NM alloy. Silver, as the main constituent of the alloy according to the invention, fixes the basic mechanical and chemical properties. Due to the high silver content, the CTE of the alloy that can be fired onto, according to the invention can be matched to the CTE of highly expanded ceramics, so-called LFC (low fusing ceramic) materials. The proportion of silver in an alloy according to the invention is advantageously 40-44 wt. %, preferably 40.3-43.0 wt. %.

[0020] In an alloy according to the invention, the proportion of gold is 38-42 wt. %, but preferably 38-40 wt. %. Due to the high miscibility of gold and silver, a homogeneous

crystal structure and the solidification of mixed crystals occur in an alloy according to the invention. Due to the more noble character of gold, as compared with silver, the corrosion resistance of an alloy according to the invention is especially high. In addition, the proportion of gold leads to an optimised colour effect; a polished surface of an alloy according to the invention exhibits a pleasant warm tone.

[0021] The proportion of palladium in an alloy that can be fired onto, according to the invention is in the range 0-14.5 wt. %. The proportion of palladium in an alloy according to the invention is preferably in the range 12.5-14.5 wt. %. The addition of palladium increases (i) the mechanical strength of the alloy and (ii) the position of the melting interval. A palladium content of more than 14.5 wt. %, however, would have an unacceptable discolouring effect and would make a yellowish-warm tone impossible to achieve.

[0022] Use of the preferred concentration ranges for silver, gold and palladium, independently of each other, leads to particularly advantageous alloys according to the invention. However, alloys according to the invention in which each of the elements silver, gold and palladium has a concentration in the ranges previously cited as preferred, are particularly preferred.

[0023] The total proportion of indium, zinc, tin, copper, lanthanides, scandium and lanthanum in an alloy according to the invention is in the range 5.5-15 wt. %. Within this range, these elements contribute to increasing the mechanical strength of the silver-gold-palladium base of an alloy according to the invention to the required value. Moreover, a more favourable adhesive bond to conventional facing ceramics can be produced with an alloy according to the invention due to the proportion of elements mentioned as present in the alloy according to the invention. Furthermore, the elements mentioned increase the hardness of the alloy in a desired manner.

[0024] On the other hand, a proportion of more than 15 wt. % of the elements mentioned would lead to unacceptably high brittleness of the final product (cast item) and, in the case of a dental framework, to the formation of oxide layers on the melt that would hamper determination of the casting point. In addition, if the proportions of the elements mentioned were much higher than those present according to the invention, multi-phase structures would be formed, in particular palladium-containing phases. Such phases tend to form dark discolorations over time in the oral cavity; therefore the formation of these has to be suppressed. Also, if there were too high a proportion of the elements mentioned, the coefficient of thermal expansion of a corresponding alloy would, in many cases, be affected in an unfavourable manner, which would lead to incompatibility with conventional dental ceramics.

[0025] The use of less than 5.5 wt. % of the elements mentioned, indium, zinc, tin, copper, lanthanides, scandium and lanthanum would no longer lead to the desired effects mentioned above (effect on hardness, strength and adhesive bond).

[0026] The proportion of the elements mentioned in an alloy according to the invention is preferably in the range 5.5-10 wt. %. The negative effects of high concentrations of these elements start to become evident at proportions above 10 wt. %.

[0027] The use of indium is preferred; an alloy according to the invention therefore contains 5.5-15 wt. %, preferably 5.5-10 wt. % of indium. An alloy according to the invention then preferably contains no zinc, tin, copper, lanthanides, scandium or lanthanum.

[0028] An alloy that can be fired onto according to the invention contains a proportion of manganese in the range 0.1-5 wt. %. Manganese functions as an oxygen trap, an adhesive oxide producer and a desulfurising agent. It also provides a beneficial oxide colour. Moreover, manganese contributes to ensuring that the viscosity of a melt of an alloy according to the invention is low enough. In addition, high strength and good polishability of the alloy is achieved by the presence of manganese. Smearing of an alloy according to the invention during the polishing process, as is observed in the case of some alloys with a high gold content, does not occur, due to the presence of manganese.

[0029] A proportion of manganese of more than 5 wt. % would lead to an undesirable increase in the CTE of a corresponding alloy (one not according to the invention) and to less beneficial casting characteristics. In addition, too high a manganese content can lead to undesirable reaction with the encapsulating material used during casting or with the ceramic being fired on. Eutectic compounds with silicon can be produced. These are coloured brown due to the inclusion of manganese dioxide (=brownstone) and can diffuse right into the ceramic and thus would impair the aesthetic appearance.

[0030] A proportion of manganese of less than 0.1 wt. % would lead to the previously mentioned functions of manganese in an alloy according to the invention no longer being fully achieved in individual cases.

[0031] The proportion of manganese in an alloy according to the invention is preferably 0.1-1 wt. %.

[0032] An alloy according to the invention contains a total proportion of tantalum, platinum, iridium, osmium, ruthenium, rhodium, rhenium, titanium, niobium, zirconium, tungsten and vanadium within the range 0.05-5 wt. %. The elements mentioned act as grain refiners and contribute to the high mechanical strength of the alloy according to the invention. However, in concentrations of more than 5 wt. % they would increase the brittleness of a corresponding alloy (one not according to the invention) in an unacceptable manner. In fact, the proportion of the metals mentioned in an alloy according to the invention should preferably be not more than 0.2 wt. %; the desired effects occur even at this type of low concentration.

[0033] The use of tantalum is particularly preferred; therefore, an alloy according to the invention preferably contains 0.05-5 wt. % of tantalum. In fact advantageously only 0.05-0.2 wt. %.

[0034] An alloy according to the invention preferably contains a total of not more than 1 wt. % of zinc, tin, copper, lanthanides, scandium, lanthanum, platinum, iridium, osmium, ruthenium, rhodium, rhenium, titanium, niobium, zirconium, tungsten and vanadium.

[0035] A particularly preferred alloy according to the invention consists of:

Silver	40.5 ± 2 wt. %
Gold	38.1 ± 1.5 wt. %
Palladium	13.0 ± 1 wt. %
Indium	8.0 ± 1 wt. %
Manganese	0.3 ± 0.2 wt. %
Tantalum	0.1 ± 0.03 wt. % and
other constituents	0–1 wt. %

[0036] The following composition produces a very particularly preferred embodiment of an alloy according to the invention:

Silver	40.5 wt. %
Gold	38.1 wt. %
Palladium	13.0 wt. %
Indium	8.0 wt. %
Manganese	0.3 wt. %
Tantalum	0.1 wt. %

[0037] The following alloy properties were determined for the very particularly preferred alloy according to the invention:

Density [g/cm ³]	approx. 11
Vickers hardness [HV 5]	210
Modulus of elasticity [GPa]	120
Offset yield strength (R _p 0.2) [MPa]	491
Tensile strength [MPa]	663
Elongation at break [A5] [%]	6.9
Melting interval [° C.]	975–1030
Casting temperature [° C.]	approx. 1200
CTE [10 ⁻⁶ K ⁻¹] 25–500° C.	16.97
CTE [10 ⁻⁶ K ⁻¹] 25–600° C.	17.44

[0038] This is therefore a type 4 noble metal alloy in accordance with EN ISO 8891:2000. A person skilled in the art will preferably choose the alloy constituents to produce an alloy according to the invention in such a way that the requirements in EN ISO 8891:2000 are complied with.

[0039] In addition, alloys according to the invention regularly satisfy the requirements in DIN EN ISO 9693:2000, this relating to the production of ceramic dental restorations that can be fired onto, (see also the example given below).

[0040] The alloy according to the invention, in particular in a preferred development, is characterised especially positively by the following properties

[0041] high fitting accuracy of the frameworks cast from the alloy (dental restorations);

[0042] particularly good working and finishing properties;

[0043] high resistance to corrosion;

[0044] beneficial casting point detection (a dental engineer can see when he has to start the casting process);

[0045] narrow melting interval (advantageous during the melting process; low risk of demixing during solidification process)

[0046] alloy forms low-viscosity melts;

[0047] melts of the alloy according to the invention have beneficial flow properties (this results in the melt having a high capacity to fill a mould);

[0048] the alloy can be faced with all currently used facing plastics;

[0049] the alloy can be faced with facing ceramics that have a CTE in the range 15-17 [10⁻⁶K⁻¹]

[0050] When being faced with ceramic, the alloy according to the invention has the following advantages:

[0051] favourable CTE;

[0052] good chemical adhesion (indium and manganese have an advantageous effect here);

[0053] high thermal resistance (a framework made from the alloy according to the invention does not distort during the firing process);

[0054] any normal commercially available ceramic with a CTE in the range 15-17 [10⁻⁶K⁻¹] can be used;

[0055] inexpensive

[0056] The invention also provides ceramic-faced dental restorations, containing:

[0057] a dental structure made from an alloy according to the invention as well as a dental ceramic with a CTE in the range 15-17 [10⁻⁶K⁻¹] fired onto the dental structure.

[0058] Finally, the invention also provides use of an alloy according to the invention for producing a ceramic-faced dental restoration.

[0059] With regard to the two last-mentioned aspects of the invention (dental restorations; use) the preceding comments apply with regard to preferred developments of alloys according to the invention.

[0060] The invention is described in more detail in the working example given below:

WORKING EXAMPLE

1. Producing an 8-Unit Bridge Framework:

[0061] An 8-unit upper jaw bridge was modelled out of wax; an actual patient situation was used as the model. The minimum wall thickness was 0.4 mm in each case. The anatomical moulds took into account the fact that the major part of the restoration would later, after casting, consist of metal.

[0062] The wax model was invested (encapsulated) in a phosphate-bonded investment material.

[0063] The resulting muffle was then heated to a temperature of 900° C. (preheating temperature) and held there for 60 min.

[0064] Casting was performed in an induction-heated vacuum-compression casting machine (Nautilus® MC+/Fa. BEGO, Program 290) using ingots of an alloy according to the invention with the following composition:

Silver	Ag	40.5 wt. %
Gold	Au	38.1 wt. %
Palladium	Pd	13.0 wt. %
Indium	In	8.0 wt. %
Manganese	Mn	0.3 wt. %
Tantalum	Ta	0.1 wt. %

[0065] The ingots were heated in a conventional manner. Casting was started manually about 10 s after immersion of the last solid constituents of the ingots in the melt. The casting point was recognised very easily by using melt powder, because a temporarily present oxide skin obviously broke apart.

[0066] After cooling the muffle, the investment material was removed by coarse mechanical means. The bridge framework obtained was then blasted at 2 bar with corundum with a grain size of 110 μm (Korox® 110/Fa. BEGO). Then the surface of the bridge framework was processed with a fine-toothed carbide milling cutter. Due to the low hardness and the good machinability (workability) of the alloy used, this process proved very convenient for the dental engineer.

processing instructions of the ceramic manufacturer (Vita). The temperatures and times used are given in the table below. The kiln was a Vakumat 300 (Vita).

[0073] Firings of the type “shoulder matrix firing with margin” and “glaze firing with accentuating fluid” (after opaque firing) were not used in the context of the working example. However these types of firing may be used to complete the process.

[0074] In accordance with the table given below, the following supplementary firings were performed: oxide firing, wash firing (1st opaque firing), opaque firing (2nd opaque firing), 1st dentine firing, 2nd dentine firing, corrective firing and glaze firing. Once again, ceramic materials of the Response type (Vita company) were used.

[0075] The bonding strength was determined in in-vitro tests (spalling test, quenching test and bending test in accordance with DIN EN ISO 9693:2000). All the requirements were clearly exceeded.

[0076] The non-veneered sections (edges of the crowns, but also non-veneered crowns) could be polished very easily. The rapidly achieved gloss satisfied all the demands with regard to aesthetics and offered high resistance to the adhesion of e.g. food residues and the formation of plaque.

[0077] Table of parameters used for ceramic firings:

Firing	Preheating temperature [° C.]	Residence time [min]	Heating time [min]	Rate of heating [° C./min]	Final temperature [° C.]	Residence time [min]	Total vacuum time [min]
Wash firing	400	—	4	55	780	10	16:54
opaquer (Matrix)	400	2	4	55	800	1	8:05
1st dentine firing	400	2	6	55	790	1	7:05
2nd dentine firing	400	6	6	55	770	1	6:43
Corrective firing	400	6	6	55	770	1	6:43
Glaze firing	400	—	4	55	770	1	—

[0067] The fit of the structure was equal to that of alloys with a high gold content. Joining (soldering or laser-welding) is possible.

2. Veneering the Bridge Framework with Dental Ceramic Using Wash and Opaque Firing:

[0068] Oxide firing was performed (10 min at 780° C.) in order to produce a homogeneous surface enriched with indium and manganese as adhesive oxides.

[0069] Before ceramic veneering, the surface of the bridge framework (from 1 above) was again blasted and steam-cleaned as described under 1 in order to condition the surface for subsequent wash firing.

[0070] Wash firing was performed after the application of a thin suspension of a veneering ceramic of the Response type (Vita company). The suspension did not cover the surface completely.

[0071] Opaque (matrix) firing was then performed, after the application of a covering layer of powder-opaquer of the Response type (Vita company).

[0072] Unless stated otherwise here, the procedure used for wash and opaque firing was in accordance with the

I claim:

1. An alloy that can be fired onto, for producing ceramic-faced dental restorations, comprising or consisting of:

Silver	40–45 wt. %
Gold	37.5–45 wt. %
Palladium	0–14.5 wt. %
Indium, zinc, tin, copper,	in total 5.5–15 wt. %
Lanthanides, scandium, lanthanum	
Manganese	0.1–5 wt. %
Tantalum, platinum, iridium, osmium	in total 0.05–5 wt. %
ruthenium, rhodium, rhenium,	
titanium, niobium, zirconium, tungsten,	
vanadium	
Gallium, iron	0–5 wt. %
Other metals, semimetals and impurities	0–1 wt. %

wherein the data relating to percentage by weight are each with respect to the total weight of the alloy.

2. An alloy according to claim 1, containing:

Silver and/or Gold and/or Palladium	40.3-43.0 wt. % 38-42 wt. % 12.5-14.5 wt. %.
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3. An alloy according to claim 1, containing:

Indium, zinc, tin, copper, lanthanides, scandium, lanthanum	in total 5.5-10 wt. %.
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4. An alloy according to one of claims 1 to 3, containing:

Indium	5.5-10 wt. %
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5. An alloy according to one of claims 1 to 3, containing:

Manganese	0.1-1 wt. %.
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6. An alloy according to one of claims 2 or 3, containing:

Tantalum, platinum, iridium, osmium, ruthenium, rhodium, rhenium, titanium, niobium, zirconium, tungsten, vanadium	in total 0.05-0.2 wt. %.
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7. An alloy according to one of claims 2 or 3, containing:

Tantalum	0.05-0.2 wt. %.
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8. A ceramic-faced dental restoration, comprising:

a dental structure made of an alloy according to one of claims 1-3; and

a dental ceramic with a CTE in the range 15-17 [10⁻⁶K⁻¹] fired onto the dental structure.

9. An alloy comprising:

between 38.5 and 42.5 wt. % silver;

between 36.6 and 39.6 wt. % gold;

between 0 and 14.5 wt. % palladium;

between 5.5 and 15 wt. % indium;

between 0.1 and 5 wt. % manganese; and

between 0.05 and 5 wt. % total of one or more of tantalum, platinum, iridium, osmium, ruthenium, rhodium, rhenium, titanium, niobium, zirconium, tungsten or vanadium.

10. An alloy according to claim 9 containing 0.05% to 0.2 wt. % tantalum.

11. An alloy according to claim 9 containing 12 to 14 wt. % palladium.

12. An alloy according to claim 9 containing 7 to 9 wt. % indium.

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