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(54) Title: GOLD ALLOY AND METHOD FOR MANUFACTURING A DENTAL RESTORATION

(57) Abstract: The present invention relates to an alloy with a high gold content. This alloy preferably comprises more than 99 wt.% gold. Further, the invention relates to a method for manufacturing a metal-ceramic dental restoration by pressing on or firing on of a suitable porcelain. The porcelains used here have a certain maximum processing temperature and a coefficient of thermal expansion in a certain range.

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Title: Gold alloy and method for manufacturing a dental restoration

The invention relates to a gold alloy and more in particular to a gold alloy having a high gold content. The invention further relates to a method for manufacturing a metal-ceramic dental restoration.

For a number of decennia, gold alloys with a high gold content have been used in dental restorations, particularly because of their biological and chemical inertia and their attractive deep yellow color.

For aesthetical reasons, these alloys are fired on with porcelain. This porcelain was manually built up in layers. In recent years, ceramic is also pressed on. This pressing procedure comprises the following steps: a supporting structure from a metal alloy is, either provided with a thin coating layer or not, pressed over with a press ceramic by use of the "lost wax method". During the burning out or drying out of the wax, while heating for a long time at a relatively high temperature, with many alloys, a thick oxide layer is formed on the alloy. In many cases, this oxide layer results in a dark edge or contour.

From an aesthetic point of view, steps need to be taken to form as little oxide as possible on the surface of the structure from the metal alloy.

However, for a good bond between press ceramic and metal alloy structure, an oxide layer is highly desired.

Therefore, there is a need for a high gold alloy with a solidus temperature which is sufficiently high in relation to the application temperature of the ceramic – and is, as a rule, at least 50°C higher than the firing temperature or pressing temperature of the ceramic or porcelain, which alloy forms an oxide layer upon heating in air, which layer is necessary for a good bond with the porcelain to be fired on or pressed on, and which oxide layer is hardly or not visible.

According to the invention, an alloy with a high gold content, a so-called "high gold alloy" has now been found which remains yellow upon oxidation, which alloy is suitable for use in a metal-ceramic system, in which a gold alloy with an aesthetic yellow color is fired on or pressed on with a dental ceramic or porcelain tailored thereto. In addition, the alloy according to the invention has a high degree of biocompatibility.

This alloy according to the invention comprises 0.01-0.05 wt.% zinc; 0.01-0.05 wt.% indium; 0.01-0.05 wt.% silver and 0.01-0.05 wt.% manganese in a gold base.

The gold base substantially consists of gold, but may contain small amounts of pollutants, as long as they produce no adverse color effects and do not affect the biocompatibility.

In a preferred embodiment, the alloy according to the invention comprises at least 99 wt.% gold. A very suitable alloy substantially consists of 99.80 wt.% gold; 0.05 wt.% zinc; 0.05 wt.% indium; 0.05 wt.% silver and 0.05 wt.% manganese.

With the high gold alloy according to the invention, it has been found possible to fire or press it with ceramic, while the intense gold color is preserved.

The alloy according to the invention provides a stable, very thin, possibly monomolecular oxidation layer which is so light in color than no adverse color effects occur. However, the oxidation layer is sufficiently strongly bound to the underlying alloy and appears to be capable of a very good metal-press glass or metal-porcelain binding.

Particularly the presence of manganese provides a good bond. Tin and indium ensure a reinforcement of the oxide. Incidentally, the gold alloy according to the invention does not have a very great strength, but this has not been found necessary for the applications for which this alloy is intended.

The alloys according to the invention have a solidus temperature of between 1030 and 1100°C; for the preferred alloys, the solidus temperature is between 1045 and 1065°C. For the alloys according to the invention, the coefficient of thermal expansion (measured from 25 to 500°C) is between 14.5 and 15.5 μm/m.°C; and for the preferred alloys between 14.8 and 15.3 μm/m.°C.

High gold alloys were already known in the state of the art. For instance, DE-OS 44 19 408 describes a dental alloy with 95-98 wt.% gold; 1-4 wt.% titanium; and 0.05-1.5 wt.% of one or more elements from the group of Re, Rh, Ru, Ir and Ta.

Further, US-A-5,922,276 relates to a dental alloy with an excellent oxide color, which alloy contains at least 99.5 wt.% gold, 0.1-0.25 wt.% zinc, 0.1-0.25 wt.% indium and up to 0.3 wt.% Rt, Pd, Rh, Ir, Re or combinations thereof. It is explicitly stated that elements like copper, manganese and iron should be avoided because they produce dark or colored oxides.

Further, the invention relates to a method for manufacturing a metal-ceramic dental restoration, comprising pressing, with heating, a tooth-colored press glass onto a wholly or partly supporting structure from the alloy according to the invention, with the press glass having a coefficient of thermal expansion (CTE) of between 12.5 and 14.5, and preferably between 13.0 and 14.5 km/m.K, measured in the range from 25°C to 500°C or to the glass transformation temperature, depending on which of the two is the lowest, and with the press glass having a pressing temperature which is at least 50°C lower than the solidus temperature of the alloy.

In this method, the press glass is pressed with heating in a mold manufactured by use of the "lost wax" method. Such a method is much more effective and economical than the conventional method in which porcelain was applied layer by layer. In addition, fewer bubbles and cracks are formed during pressing compared to applying the porcelain layer by layer.

Incidentally, the alloy according to the invention can also be coated with this conventional method.

In more detail, in the pressing method according to the invention, a wax model of one or more teeth and/or molars is made, which model is embedded in a fire-resistant material, for instance *Carrara* ® *Universal Dustless Investment* (*ex* Elephant Dental B.V., Hoorn, The Netherlands). Then, after curing of the die from fire-resistant material, the wax is burnt out. After this, a closed pellet of press glass is brought, on the connecting channels, to the mold, by pressing the glass therein with a fire-resistant cylinder with thermal plasticization. In the die, the structure from the high gold alloy according to the invention is present, as stated. This structure may, for instance, be formed by CAD/CAM methodologies.

Preferably, the press glass is available in a tooth color. The coloring of porcelain is known to a skilled person. A suitable method is described in DE-OS-1999 04 522, which document is understood to be inserted in this specification for the description of the coloring method.

In a preferred embodiment, before the pressing, first, a so-called liner may be applied onto the alloy. This liner will, as a rule, have a melting point which is less than 50°C lower than the pressing temperature of the press glass. A suitable liner consists of 58.5 wt.% SiO_2, 12.6 wt.% Al_2O_3, 11.0 wt.% K_2O, 7.1 wt.% Na_2O, 10.4 wt.% CeO_2, 0.4 wt.% LiO_2. This liner can be applied as a single coating in a thickness of 20-40 μm and be burnt up at about 900°C.

A suitable press glass may have the following (preferred) composition: 7-15 wt.% Al_2O_3; 13-23 wt.% (K_2O + Na_2O), 1-3 wt.% (BaO + CaO), 1-3 wt.% (Sb_2O_3 + Li_2O) and 0.2-1.2 wt.% fluorine, rest SiO_2 including coloring compositions. 7-15 wt.% Al_2O_3; 6-14 wt.% K_2O, 5-11 wt.% Na_2O, 0.2-2.5 wt.% BaO, 0.1-1.5 wt.% CaO, 1.2-2.5 wt.% Sb_2O_3, 0.05-0.5 wt.% Li_2O and 0.5-1.0 wt.% fluorine, rest SiO_2 including coloring compositions.

The powder formed from these glass compositions preferably has a particle size smaller than 106 μm. This powder is granulated with a binder and uniaxially dry-pressed at room temperature and sintered at a temperature of, for instance, 800-1000°C, preferably 900-960°C, for 1 minute to 1 hour, preferably 1-30 minutes.

In addition, the invention relates to a method for manufacturing a metal-ceramic dental restoration, comprising firing a dental porcelain onto a supporting structure from the alloy according to any one of claims 1-3, with the porcelain having a coefficient of thermal expansion of between 12.5 and 14.5 μm/m.K, measured in the range from 25°C to 500°C or to the glass transformation temperature, depending on which of the two is the lowest, and with the porcelain having a firing temperature which is at least 50°C lower than the solidus temperature of the alloy. A suitable firing ceramic has the following (preferred) composition: 64.1-67.0% SiO_2, 11.0-12.5% Al_2O_3, 10.1-11.6% K_2O, 6.6-8.6% Na_2O, 0.7-1.1% CaO, 0.4-1.3% BaO, 0-2.1% Sb_2O_3, 0-0.2% Li_2O, and 0-0.6% fluorine with pigments. A more preferred firing ceramic has the following composition: 64.1% SiO_2, 14.2% Al_2O_3, 11.1% K_2O, 6.6% Na_2O, 1.1% CaO, 0.4% BaO, 1.4% Sb_2O_3, 0.2% Li_2O and 0.6% F_2 with pigments.

Every CTE described in this specification or the claims is measured in the range from 25°C to 500°C or to the glass transformation temperature, depending on which of the two is the lowest. Also, every percentage is a weight percentage related to the weight of the total composition, unless indicated otherwise.

The pressing or firing temperature needs to be at least 50°C lower than the solidus temperature of the alloy in order to avoid deformation of the metal structure during pressing. The CTE of the press glass or porcelain needs to be such that the CTE of the alloy is 0.5-2.0 μm/m.K higher than that of the press glass or porcelain. When the difference is greater than 2.0 μm/m.K, cracking in the porcelain may occur; when the difference is

smaller than 0.5 μm/m.K, possibly, a structure is obtained in which the bond between press glass or the porcelain and alloy is insufficient. In the range mentioned, the porcelain is subjected to such pressure after cooling that a strong restoration is obtained.

The invention will now be illustrated in more detail in and by the following non-limiting examples.

Example 1 (comparative)

Into a crucible of pure alumina, in a vacuum induction furnace, the following metals were weighed and melted under a partial pressure of 400 Torr of argon gas and then cast to a bar in a die which had already been present in the vacuum chamber: 97.625 wt.% gold, 1.5 wt.% platinum, 0.5 wt.% zinc, 0.375 wt.% rhodium. After casting, the die was removed from the vacuum induction furnace and the die was opened.

The bar was rolled out to plate with, optionally, glowing between whiles to bring the plate back into a rollable condition. After this, the plate was cut into strips and the alloy was cut into cubes.

The alloys were then cast in an electric casting device at 1200°C into a graphite-containing, phosphate-bound embedding mass die, which had been preheated to 750°C. After oxidation, the alloy has a grey-yellow color.

The binding with porcelain is given in Table 3.

Example 2 (comparative)

In the same manner as in Example 1, an alloy was produced with the following composition: 98.2 wt.% gold, 1.2 wt.% platinum, 0.1 wt.% zinc, 0.3% rhodium and 0.2% indium. After oxidation, the alloy has a grey-yellow color.

Example 3

In the same manner as in Example 1, an alloy was produced with the following composition: 99.8 wt.% gold, 0.05% zinc, 0.05% indium, 0.05% silver, 0.05% manganese. After oxidation, the alloy has an intensely yellow color.

Example 4 (comparative)

In the same manner as in Example 1, an alloy was produced with the following composition: 99.7 wt.% gold, 0.1% zinc, 0.2% indium (see US-A-5,922,276). After oxidation, the alloy has an intensely yellow color, but did not have the good bond of Example 3.

Results of Examples 1-4 are shown in the following Table.

Metal component	Example number (wt.% components)			
	1	2	3	US 5922276
Gold	97.625	98.2	99.8	99.7
Platinum	1.5	1.2	-	-
Iridium	-	-	-	-
Zinc	0.5	0.1	0.05	0.1
Indium	-	0.5	0.05	0.2
Silver	-	-	0.05	-
Manganese	-	-	0.05	-
Rhodium	0.375	0.3	-	-
Tensile strength, MPa	180	160	133	142
Yield point, MPa	79	63	51	54
Elongation at break, %	23.4	31.9	53	34
Vickers hardness, HV	75	43	37	38
Liquidus, °C	1080	1070	1060	1060
Solidus, °C	1060	1050	1050	1050
Coefficient of thermal expansion (20-500°C) µm/m.°C	15.3	15.1	15.0	15.1
Oxidation color	yellow/ grey	yellow/ grey	yellow	yellow
Binding porcelain, %	75	71	70	61
Binding press ceramic, %	71	73	72	63

A round disk of the alloys was cast with a diameter of 25 mm and a thickness of 1.0 mm. After casting, the casting pieces were ground with coarse and fine aluminum oxide. The metal-ceramic disk was then deformed

from the top, with the porcelain downwards, by a stamp with a spherical end. The disk was bent 0.4 mm in the centre to achieve a consistent deformation of the disk and removal of the ceramic with minimal cracks in the metal. After the breaking off of the porcelain, loose particles of porcelain were removed from the surface of fracture with a nylon brush, after which the surface of fracture was placed in an ultrasonic bath for 10 minutes.

After breaking, the samples were tested for the amount of remaining porcelain surface by means of a scanning electron microscope. The percentage of oxidized metal surface which was still coated with ceramic was measured by measuring the amount of silicon on the surface of fracture by means of E.D.A.X. and comparing this to the uncovered part of metal surface and a surface 100% covered with porcelain. The average surface fractions or remaining ceramic were given in the above Table. The values for remaining surface still covered with porcelain show that the majority is still attached to the alloy after the breaking off of the mass of the porcelain. Tests of other alloy systems have shown that a percentage higher than 50% does not cause problems in practice.

CLAIMS

1. An alloy comprising 0.01-0.05 wt.% zinc; 0.01-0.05 wt.% indium; 0.01-0.05 wt.% silver; 0.01-0.05 wt.% manganese; and rest gold basis.

2. An alloy according to claim 1, comprising 99 wt.% gold.

3. An alloy according to claim 1 or 2, substantially consisting of 99.80 wt.% gold; 0.05 wt.% zinc; 0.05 wt.% indium; 0.05 wt.% silver and 0.05 wt.% manganese.

4. A method for manufacturing a metal-ceramic dental restoration, comprising pressing, with heating, a tooth-colored press glass onto a wholly or partly supporting structure from the alloy according to any one of the preceding claims, wherein the press glass has a coefficient of thermal expansion of between 12.5 and 14.5 μm/m.K, measured in the range from 25°C to 500°C or to the glass transformation temperature, depending on which of the two is the lowest, and wherein the press glass has a pressing temperature which is at least 50°C lower than the solidus temperature of the alloy.

5. A method for manufacturing a metal-ceramic dental restoration, comprising the firing a dental porcelain onto a supporting structure from the alloy according to any one of claims 1-3, wherein the porcelain has a coefficient of thermal expansion of between 12.5 and 14.5 μm/m.K, measured in the range from 25°C to 500°C or to the glass transformation temperature, depending on which of the two is the lowest, and wherein the porcelain has a firing temperature which is at least 50°C lower than the solidus temperature of the alloy.

INTERNATIONAL SEARCH REPORT

Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C22C5/02 A61K6/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C22C A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	NL 9 200 564 A (ELEPHANT EDELMETAAL BV) 18 October 1993 (1993-10-18) the whole document	4,5
A		1-3
A	DE 195 25 361 A (HERBST BREMER GOLDSCHLAEGEREI) 22 August 1996 (1996-08-22) the whole document	1-5
A	EP 1 193 320 A (CENDRES & METAUX SA) 3 April 2002 (2002-04-03) the whole document	1-5
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 015, no. 337 (C-0862), 27 August 1991 (1991-08-27) & JP 03 130332 A (TOKURIKI HONTEN CO LTD;OTHERS: 01), 4 June 1991 (1991-06-04) abstract -----	

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