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Prasad et al.(10) **Pub. No.: US 2010/0119400 A1**(43) **Pub. Date: May 13, 2010**(54) **HIGH NOBLE DENTAL ALLOY****Publication Classification**(76) Inventors: **Arun Prasad**, Cheshire, CT (US);
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B22F 9/00 (2006.01)(52) **U.S. Cl. 419/1; 420/463; 420/580; 75/352**(21) Appl. No.: **12/617,381**(22) Filed: **Nov. 12, 2009****Related U.S. Application Data**(60) Provisional application No. 61/113,917, filed on Nov.
12, 2008.(57) **ABSTRACT**

A silver free high noble dental alloy comprising at least 60 wt. % noble materials, where 40 wt. % of the material is gold; at least 2.5 wt. % gallium, at least about from 2 to 4 wt. % cobalt; and at least from about 0.01 to 0.25 wt. % lithium and/or boron; and a principal balance of palladium is provided. Dental products and methods of manufacturing dental products using such a high noble dental alloys are also provided.

HIGH NOBLE DENTAL ALLOY**CROSS-REFERENCE TO RELATED APPLICATIONS**

[0001] This application claims priority to U.S. Provisional Patent Application No. 61/113,917, filed Nov. 12, 2008, the disclosure of which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] This invention concerns a silver free, high noble dental alloy (as defined by American Dental Association's classification of alloys, i.e., alloys containing at least 60 wt. % noble metal content where at least 40 wt. % of the noble metal content is gold) for use with porcelains-fused to-metal and crown and bridge casting techniques

BACKGROUND OF THE INVENTION

[0003] Dental alloys employed in the porcelain-fused-to-metal processing technique may be classified into several groups, including noble alloys and high noble alloys. The cost of the alloy is dependent upon the commodity prices of the alloy components. For example, as of November, 2008 the costs of the major components of such alloys are: gold \$734 per Troy ounce, palladium \$ 199 per Troy ounce; cobalt \$1 per Troy ounce; and nickel \$0.3 per Troy ounce. The economic advantage of using as little of the high cost gold or palladium metals is immediately obvious. In general, however, silver is used as a replacement in alloys with reduced gold content because its properties are very compatible with gold.

[0004] Unfortunately, the presence of silver can itself lead to other problems, including the difficulty found in matching the coefficient of thermal expansion (CTE) of silver to most commercially available porcelains, and the strong tendency that silver has to react with its surrounding, which can lead to an unacceptable level of discoloration in the porcelain of the dental device. As a result, significant effort has been exerted to find high noble content alloys that are silver free while still being compatible with conventional dental porcelains.

[0005] A detailed analysis of commercially available silver-free alloys worldwide reveals that there are no silver free alloys with the lowest level of Au needed for high noble (HN) classification (i.e., noble metals (Au+Pt Groups) ≥ 60 wt % with the proviso that Au ≥ 40 wt %). It is to be noted that silver-free alloys having Au concentrations either ≥ 45 wt. % or ≤ 35 wt. % are available. (See, e.g., U.S. Pat. Nos. 4,123,262; 4,179,286; 4,539,176 and 4,591,483.) However, the latter alloys suffer from being classified as lower category noble (N) alloys (i.e., alloys having a noble metal content of 25 wt. %), and the former alloys require the use of excessive amounts of Au, which render these alloys costly to use. Thus, there is a need for a silver free HN alloy with a concentration of Au that is as low as possible (~ 40 wt. %).

BRIEF SUMMARY OF THE INVENTION

[0006] Thus, there is provided in the practice of this invention according to a presently preferred embodiment, a workable HN dental alloy comprising at least 60 wt. % noble metal, where from about 40 to 44 wt. % of the noble metal is gold, and where the principal balance of the alloy, absent small contributions from additives, is palladium. The alloy further comprises at least 2.5 wt. % gallium, from about 2 to 4 wt. % cobalt and from about 0.01 to 0.25 wt. % lithium

and/or boron to extend the use of the alloy with porcelains having wider coefficients of thermal expansions (GTE).

[0007] In another embodiment of the invention the alloy may include about 6 wt. % of a combination of one or more of germanium, gallium, tin, indium, zinc and manganese, where the amount of gallium is ≥ 2.5 wt. %.

[0008] In yet another embodiment of the invention the alloy may include up to about 1 wt. % of one or more of ruthenium, rhenium and iridium.

[0009] In still another embodiment of the invention the alloy composition comprises 40 wt. % gold; 50.7 wt. % palladium; 3 wt. % gallium; 3 wt. % tin; 3 wt. % cobalt; 0.1 wt. % ruthenium; 0.1 wt. % rhenium; and 0.1 wt. % lithium.

[0010] In still yet another embodiment the invention is directed to a dental product fabricated using the alloy described above.

[0011] In still yet another embodiment the invention is directed to a method of manufacturing a dental product fabricated from the alloy (or its powder) described above using a technique selected from casting, molding, milling or laser sintering.

DETAILED DESCRIPTION OF THE INVENTION

[0012] A high noble dental alloy is considered to be one with at least 60 wt. % noble metal content, the noble metals include ruthenium, platinum, palladium, iridium, osmium, rhodium and gold, where the content of gold must comprise at least 40 wt. % of the alloy. The alloy provided herein is a high noble alloy for use with high coefficient of thermal expansion (CTE) porcelains that contains the minimum possible concentration of gold. The alloy accomplishes this dual function by having more than 60 wt. % palladium and gold, where the gold only constitutes from around 40 to 44 wt. % of the total, at least 2.5 wt. % gallium, from 2 to 4 wt. % cobalt and 0.01 to 0.25 wt. % (lithium and/or boron). It should be noted that unless otherwise indicated all percentages herein are by weight.

[0013] The choice of palladium has both metallurgical and economic benefits. For example, consider the price of gold and the platinum group metals as of November 2008:

Rhodium	\$1600
Platinum	\$ 838
Gold	\$ 734
Iridium	\$ 440
Ruthenium	\$ 235
Palladium	\$ 199

Palladium has a lower cost relative to the other platinum group metals so there is an economic advantage to maximize the palladium content in place of gold and the other platinum group elements.

[0014] From a metallurgical perspective, palladium acts as an alloy strengthener, is a thermal expansion adjuster for the alloys (to better match thermal expansion of dental porcelains) and reduces the alloy's oxidation rate. The palladium also protects the alloy from corrosion. The palladium serves to enable the alloy to protect the alloy from adverse reactions. The current application identifies a HN alloy having high palladium content suitable for dental applications that defies conventional formulations by maintaining a percentage of gold at or above 40 wt. %, but no higher than 44 wt. %.

[0015] The invention also incorporates the addition of from 2 to 4 wt. % cobalt to adjust the thermal expansion properties of the alloys in order to make them compatible with high CTE porcelains, and from 0.01 to 0.25 wt. % of one or both lithium and boron to suppress the formation of cobalt oxides that would otherwise form an unappealing dark line at the porcelain-metal junction. It was also found that for an equivalent amount, lithium is more effective than boron in this regard. Both cobalt and lithium also tend to modify the grain structure of the alloy making it more machinable. In addition, lithium is not only a deoxidizer but also a getter for hydrogen. Finally, at least 2.5 wt. % of gallium is included to lower the melting range, and improve the castability and mechanical properties of the alloys

[0016] Accordingly, an family of alloys suitable for practice of this invention would comprise at least 60 wt. % noble metal, where 40 to 44 wt. % is gold; from 2 to 4 wt. % cobalt; at least 2.5 wt. % gallium, from 0.01 to 0.25 wt. % lithium and/or boron.

[0017] Although only the essential compositional materials are described above, it should be understood that the alloy may also contain other elements to improve the metallurgical properties of the material, including up to 6 wt. % of a combination of germanium, gallium, tin, indium, zinc and manganese. Specifically, small concentrations (up to ~6 wt. %) of these materials and particularly gallium can serve to lower the melting range, and improve the castability and mechanical properties of the alloys. In a preferred embodiment, the range of these materials is from about 2.5 to 6 wt. %, but where at least about 2.5 wt % of these materials must be gallium. However, excessive amount of Ga lowers the solidus temperature to a range where distortion becomes an issue when the alloy is used against medium fusing, conventional porcelains. In addition, the alloy may contain up to about 1.0 wt. % rhenium, ruthenium and iridium for grain refinement. Finer grains eliminate hot tears during casting operations and the castings are more readily ground to a smooth and shiny finish.

[0018] A summary of the compositional ranges of both the required and optional materials is provided in Table 1, below.

TABLE 1

Compositional Ranges	
Materials	Percent Composition (wt. %)
Au	40-44
Pd	Balance
Co	2-4
Li and/or B	0.01-0.25
1 or more of: Ge, Ga, Sn, In, Zn &	2.5-~6
Mn	(where Ga is ≥ 2.5)
1 or more of: Ru, Re, & Ir	0-1

[0019] Thus in a preferred embodiment, the alloy is a HN alloy with a noble metal content of more than 60 wt. %, where gold makes up at least 40 wt. % of the noble material; about 3 wt. % gallium; about 3 wt. % tin; about 3 wt. % cobalt; about 0.1 wt. % ruthenium; about 0.1 wt. % rhenium; and about 0.1 wt. % lithium. The amount of palladium in this embodiment is preferably about 50.7 wt. %.

[0020] It is appreciated that the above compositions suitable for use with dental appliances are not exclusive. Those of skill in the art will be aware that some of the materials can be substituted or additional materials may be added without

altering the key properties of the alloys of the current invention. For example, it is well known that small amounts of palladium can be substituted with copper, nickel and iron. Alternatively, small concentrations (less than 5 wt. %) of these materials may also be added or be found in the alloy as impurities without affecting the properties of the overall composition. Ruthenium can also be substituted by Iridium.

[0021] Although the above description has focused on a range of compositions for the alloys of the current invention, the invention is also directed to dental products made from the alloys, and to methods of manufacturing dental products from the alloys. In general, such methods will include the steps of providing an alloy having a composition in accordance with the above description and then shaping that alloy using any suitable means. In this regard, the alloy of the instant invention allows for the use of a number of conventional shaping techniques, such as, casting and molding. Moreover, the alloys of the current invention also allow for the use of more recent advances in shaping technologies, such as, for example, CAD/CAM milling and selective laser sintering. It should be understood that any of these techniques or a combination thereof may be used with the alloy of the current invention.

[0022] Specifically, the alloy may be cast into blocks using traditional dental laboratory techniques or may be atomized into powders making it especially suited for use with newer CAD/CAM and powder metallurgical applications where no casting is required. In one such technique, substrates or final restorations can be milled from blocks made from these alloys. As powders, these alloys can be used either to create three dimensional preforms utilizing appropriate binders and then be sintered, or can be directly sintered/melted such as for example, with a laser, to create substrates or final restoratives. Exemplary disclosures of such processes can be found, for example, in U.S. Pat. Nos. 7,084,370 and 6,994,549, the disclosures of which are incorporated herein by reference. It should be understood that while some prior art laser sintering techniques specify a specific range of useable alloy particulate sizes, the alloys of the current invention are contemplated for use in laser sintering techniques over all possible particulate size ranges.

[0023] Those skilled in the art will appreciate that the foregoing examples and descriptions of various preferred embodiments of the present invention are merely illustrative of the invention as a whole, and that variations in the relative composition of the various components of the present invention may be made within the spirit and scope of the invention. For example, it will be clear to one skilled in the art that typical impurities and/or additives may be included in the compositions discussed above that would not affect the improved properties of the alloys of the current invention nor render the alloys unsuitable for their intended purpose. Accordingly, the present invention is not limited to the specific embodiments described herein but, rather, is defined by the scope of the appended claims.

What is claimed is:

1. A high noble dental alloy comprising:



where X is at least one material selected from the group consisting of lithium and boron;

where Y is at least one material selected from the group consisting of germanium, tin, indium, zinc and manganese;

where Z is at least one material selected from the group consisting of ruthenium, rhenium and iridium;
 where a is the sum of b, c, d, e and f; and
 where b is from 40 to 44 wt. %, c is from about 2 to 4 wt. %, d is from about 0.01 to 0.25 wt. %, e is from about 2.5 to 6 wt. % where gallium must comprise at least 2.5 wt. % of the total alloy composition, and f is from about 0 to 1 wt. %.

2. The high noble dental alloy of claim 1, where b is 40 wt. %.

3. The high noble dental alloy of claim 1, where c is about 3 wt. %.

4. The high noble dental alloy of claim 1, where d is about 0.1 wt. %.

5. The high noble dental alloy of claim 4, where X is lithium.

6. The high noble dental alloy of claim 1, where e is about 6 wt. %.

7. The high noble dental alloy of claim 6, where Y is a mixture of gallium and tin.

8. The high noble dental alloy of claim 7, where gallium comprises 3 wt. % of the alloy.

9. The high noble dental alloy of claim 1, where f is about 0.2 wt. %.

10. The high noble dental alloy of claim 9, where Z is a mixture of ruthenium and rhenium.

11. The high noble dental alloy of claim 10, where ruthenium and rhenium each comprise 0.1 wt. % of the alloy.

12. The high noble dental alloy of claim 1, wherein the alloy further comprises less than 5 wt. % of at least one trace additive selected from the group consisting of copper, nickel and iron.

13. The high noble dental alloy of claim 1, wherein the alloy comprises 50.7 wt. % palladium, 40 wt. % gold, 3 wt. % cobalt, 3 wt. % gallium, 3 wt. % tin, 0.1 wt. % lithium, 0.1 wt. % rhenium and 0.1 wt. % ruthenium.

14. A dental product comprising:

a substrate for dental application, said substrate being formed of a high noble dental alloy comprising:



where X is at least one material selected from the group consisting of lithium and boron;

where Y is at least one material selected from the group consisting of germanium, tin, indium, zinc and manganese;

where Z is at least one material selected from the group consisting of ruthenium, rhenium and iridium;

where a is the sum of b, c, d, e and f; and

where b is from 40 to 44 wt. %, c is from about 2 wt. % to 4 wt. %, d is from about 0.01 to 0.25 wt. %, e is from

about 2.5 to 6 wt. % where gallium must comprise at least 2.5 wt. % of the total alloy composition, and f is from about 0 to 1 wt. %.

15. The dental product of claim 14, where b is 40 wt. %.

16. The dental product of claim 14, where c is about 3 wt. %.

17. The dental product of claim 14, where d is about 0.1 wt. %.

18. The dental product of claim 17, where X is lithium.

19. The dental product of claim 14, where e is about 6 wt. %.

20. The dental product of claim 19, where Y is a mixture of gallium and tin.

21. The dental product of claim 20, where gallium comprises 3 wt. % of the alloy.

22. The dental product of claim 14, where f is about 0.2 wt. %.

23. The dental product of claim 22, where Z is a mixture of ruthenium and rhenium.

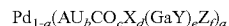
24. The dental product of claim 23, where ruthenium and rhenium each comprise 0.1 wt. % of the alloy.

25. The dental product of claim 14, wherein the alloy further comprises less than 5 wt. % of at least one trace additive selected from the group consisting of copper, nickel and iron.

26. The dental product of claim 14, wherein the alloy composition comprises 50.7 wt. % palladium, 40 wt. % gold, 3 wt. % cobalt, 3 wt. % gallium, 3 wt. % tin, 0.1 wt. % lithium, 0.1 wt. % rhenium and 0.1 wt. % ruthenium.

27. A method of forming a dental product comprising the steps of:

providing a high noble dental alloy comprising:



where X is at least one material selected from the group consisting of lithium and boron,

where Y is at least one material selected from the group consisting of germanium, tin, indium, zinc and manganese,

where Z is at least one material selected from the group consisting of ruthenium, rhenium and iridium,

where a is the sum of b, c, d, e and f, and

where b is from 40 to 44 wt. %, c is from about 2 wt. % to 4 wt. %, d is from about 0.01 to 0.25 wt. %, e is from about 2.5 to 6 wt. % where gallium must comprise at least 2.5 wt. % of the total alloy composition, and f is from about 0 to 1 wt. %; and

shaping the dental alloy to form a dental product.

28. The method of claim 27, wherein the step of shaping comprises converting the alloy into a powder.

29. The method of claim 28, wherein the step of shaping is selected from the group consisting of casting, molding, milling and laser sintering.

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