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(54) **DENTAL ALLOYS**

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(57) **ABSTRACT**

The dental alloys herein are formulated from a combination of palladium, silver and platinum and a small amount of one or more of indium, gallium, tin, germanium, zinc and manganese. The alloys may also contain one or more of gold, iridium, ruthenium, rhodium, rhenium, titanium, aluminum, silicon, hafnium, boron, and/or calcium. The alloys are particularly useful as substrate components for dental restorative materials including, but not limited to, orthodontic appliances, bridges, space maintainers, tooth replacement appliances, splints, crowns, partial crowns, dentures, posts, teeth, jackets, inlays, onlays, facing, veneers, facets, implants, abutments, cylinders, and connectors. The substrate may be defined as a main component of the dental restoration having one or more layers of material thereon, or as the complete restoration with no other material thereon.

DENTAL ALLOYS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This is application claims priority to U.S. Provisional Application No. 60/259,467, filed Jan. 3, 2001, which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] This invention relates to platinum, palladium and silver containing dental alloys.

BACKGROUND OF THE INVENTION

[0003] Gold-based alloys in dentistry were initially replaced by more economical palladium based alloys. Recent increases in the price of palladium are making these alloys very expensive. Other economical alternatives have been nickel-based, cobalt-based and titanium-based systems. Nickel-based alloys allegedly have sensitivity and toxicity concerns. Cobalt-based and titanium-based alloys are difficult to process and require special care and expensive equipment.

[0004] Prior solutions to the problem have been to use metal free ceramic/composite systems or sintered or plated copings. It is desirable to provide alloys for use in the manufacture of dental restorations having high corrosion resistance, good aesthetic qualities and good formability.

SUMMARY OF THE INVENTION

[0005] These and other objects and advantages are accomplished by the alloys herein having a coefficient of thermal expansion in the range from about 8 to about $18 \times 10^{-6}/^{\circ}\text{C}$. in the temperature range of 25-500° C. and melting temperatures above about 800° C. but below about 1500° C. The alloys contain platinum, palladium, silver and a small amount of one or more of indium, gallium, tin, germanium, zinc and manganese. The alloys may also contain one or more of gold, iridium, ruthenium, rhodium, rhenium, titanium, aluminum, silicon, hafnium, boron, and/or calcium.

[0006] The alloys are particularly useful as substrate components for dental restorative materials including, but not limited to, orthodontic appliances, bridges, space maintainers, tooth replacement appliances, splints, crowns, partial crowns, dentures, posts, teeth, jackets, inlays, onlays, facing, veneers, facets, implants, abutments, cylinders, and connectors. The substrate may be defined as a main component of the dental restoration having one or more layers of material thereon, or as the complete restoration with no other material thereon.

DESCRIPTION OF THE INVENTION

[0007] The dental alloys herein are formulated from a combination of palladium, silver, platinum and a small amount of one or more of indium, gallium, tin, germanium, zinc and manganese. The alloys may optionally contain one or more of gold, iridium, ruthenium, rhodium, rhenium, titanium, aluminum, silicon, hafnium, boron, and/or calcium. These metals serve to adjust the mechanical properties such as strength, hardness, castability and melting range. The metals are present in the ranges set forth in Table 1 below.

TABLE 1

Elements	Range (wt %)	Preferred Range (wt %)
Pt	about 6 to about 25	about 8 to about 20
Pd	about 10 to about 50	about 15 to about 50
Ag	about 15 to about 75	about 15 to about 70
Au	up to about 55	about 2 to about 52
In	up to about 10	up to about 10
Ga	up to about 10	up to about 10
Sn	up to about 10	up to about 10
Ge	up to about 10	up to about 10
Zn	up to about 10	up to about 10
Mn	up to about 10	up to about 10
In + Ga + Sn + Ge + Zn + Mn	about 0.1 to about 10	about 3 to about 10
Ir	up to about 3	up to about 1
Ru	up to about 3	up to about 3
Rh	up to about 3	up to about 3
Re	up to about 3	up to about 1
Ir + Ru + Rh + Re	up to about 3	about 0.1 to about 3
Ti	up to about 1	up to about .25
Al	up to about .25	up to about .25
Si	up to about .25	up to about .25
Hf	up to about .25	up to about .25
B	up to about .25	up to about .25
Ca	up to about .25	up to about .25
Ti + Al + Si + Hf + B + Ca	up to about 1	up to about 1
Coefficient of Thermal Expansion (25–500° C.)	$8\text{--}18 \times 10^{-6}/^{\circ}\text{C}$.	$8\text{--}18 \times 10^{-6}/^{\circ}\text{C}$.
Melting temperatures	800–1500° C.	1000–1350° C.

[0008] As can be seen in Table 1, the compositions herein contain a high percent of noble metals, i.e., a high content of Ag, Au, Pt, and Pd. The high nobility of the alloys herein minimizes the amount of oxide forming on the surface of the alloys, thereby providing less colorization and providing more esthetic alloys. The alloys herein are easier to mask and provide overall, more esthetic and more natural looking final restorations. The high content of the noble metals in the alloys herein classify the alloys into the Noble and High Noble categories of the American Dental Association (ADA) classification system for casting alloys.

[0009] The alloy is useful with low-melting dental ceramics having coefficients of thermal expansion (at 25-500° C.) in the range of about 6 to about $16 \times 10^{-6}/^{\circ}\text{C}$.

[0010] The following Table 2 sets forth examples of alloys prepared for use as dental restorative materials. The alloys herein are particularly useful as substrate components for dental restorative materials including, but not limited to, orthodontic appliances, bridges, space maintainers, tooth replacement appliances, splints, crowns, partial crowns, dentures, posts, teeth, jackets, inlays, onlays, facing, veneers, facets, implants, abutments, cylinders, and connectors. The substrate may be defined as a main component of the dental restoration having one or more layers of material thereon, or as the complete restoration with no other material thereon.

TABLE 2

Elements (wt %)	1	2	3	4
Au	50	30	13	0
Pt	8.5	10	13	12.5
Pd	17.85	32	42	12.5
Ag	19	20	24	71

TABLE 2-continued

Elements (wt %)	1	2	3	4
In	2.25	4	6.85	2.65
Sn	2.25	2	0	0
Zn	0	1.85	0	1
Ga	0	0	1	.2
Ru	0.1	0.1	0.1	.1
Ca + B	0.05	0.05	0.05	0.05
Total	100	100	100	100
CTE(25–500° C.)	14.35	14.6	14.1	16.8

[0011] The following Table 3 sets forth various properties of Alloy 1.

TABLE 3

NAME:		Alloy 1
Yield Strength/Proof Stress:	MPa	436
ISO 9693-99 Minimum = 250 MPa		
Ultimate Tensile Strength (UTS):	MPa	607
% Elongation:	%	9.4
ISO 9693-99 Minimum 3%		
Modulus of Elasticity:	GPa	111.43
Vickers Hardness:		190
Melting Range:	° C.	1165° C.–1250° C.
Casting Temp:	° C.	1350° C.
CTE @ 25–500° C.	×10 ^{−6} K ^{−1}	14.35
@ 25–600° C.	×10 ^{−6} K ^{−1}	14.59
Density:	gm/cc	14.35

[0012] The alloys herein to be used according to the invention may be processed in any known manner with techniques and auxiliary substances conventional for this purpose.

[0013] A wide variety of porcelain mixtures form desirable porcelain coatings when fused to dental alloys. Different mixtures are preferred for the different layers of the restoration. The restoration may comprise a bond layer, an opaque porcelain layer, a body layer and an incisal layer. Differences in the components used for each layer and differences in the amounts of the components enable the different layers to exhibit different optical and thermal properties.

[0014] A preferred porcelain will have a fusion range of about 725° to about 950° C. and a coefficient of thermal expansion in the range from about 6 to about 16×10^{−6}/° C.×10^{−6}/° C. in the temperature range of 25-500° C. The dental porcelain may comprise oxides including but not limited to Si, Al, K, Na, Li, Ca, Mg, Zr, Ti, Sn, Y, Ce and Eu. Some commercially available porcelain compositions useful herein include Synspar® porcelain and OPC® Lowwear™ porcelain, and Avante™ porcelain, all available from Pentron Corporation, Wallingford, Conn. and Finesse™ porcelain from Dentsply, York, Pa.

[0015] A wide variety of composites can also be used and include those made of glass fillers and resins such as BIS-GMA, TEGDMA, UDMA and PCDMA. The composites may be cured by means such as photo-initiation; chemical curing; heat curing; combinations of photo-initiation and chemical curing; and combinations of photo-initiation chemical curing and heat curing. The curing may also be conducted under water, under vacuum and under pressure of

inert gases. One such composite is Sculpture® composite available from Pentron Corporation, Wallingford, Conn.

[0016] While various descriptions of the present invention are described above, it should be understood that the various features can be used singly or in any combination thereof. Therefore, this invention is not to be limited to only the specifically preferred embodiments depicted herein. Further, it should be understood that variations and modifications within the spirit and scope of the invention may occur to those skilled in the art to which the invention pertains.

[0017] Accordingly, all expedient modifications readily attainable by one versed in the art from the disclosure set forth herein that are within the scope and spirit of the present invention are to be included as further embodiments of the present invention. The scope of the present invention is accordingly defined as set forth in the appended claims.

What is claimed is:

1. A dental alloy comprising in weight percent:

- about 15 to about 75% Ag;
- about 10 to about 50% Pd;
- about 6 to about 25% Pt;
- up to about 10% In;
- up to about 10% Ga;
- up to about 10% Sn;
- up to about 10% Ge;
- up to about 10% Zn; and
- up to about 10% Mn;

wherein one or more of In, Ga, Sn, Ge, Zn and Mn is present in the amount of about 0.1 to about 10%.

2. The dental alloy of claim 1 further comprising in weight percent:

- up to about 55% Au;
- up to about 3% Ir;
- up to about 3% Ru;
- up to about 3% Rh;
- up to about 3% Re;
- wherein one or more of Ir, Ru, Rh, and Re is present is the amount up to about 3%;
- up to about 1% Ti;
- up to about 0.25% Al;
- up to about 0.25% Si;
- up to about 0.25% Hf;
- up to about 0.25% B; and
- up to about 0.25% Ca;

wherein one or more of Ti, Al, Si, Hf, B and Ca is present in an amount up to about 1%.

3. The dental alloy of claim 1 having a coefficient of thermal expansion from 25° to 500° C. in the range of 8 to 18×10^{−6}/° C.

4. The dental alloy of claim 1 having a melting temperature in the range from about 800 to about 1500° C.

5. A dental restoration comprising:

the alloy of claim 1; and

a low-melting dental ceramic having a coefficient of thermal expansion from 25° to 500° C. in the range of 6 to $16 \times 10^{-6}/^{\circ}\text{C}$.

6. A dental alloy comprising in weight percent:

about 15 to about 70% Ag;

about 15 to about 50% Pd;

about 8 to about 20% Pt;

about 2 to about 52% Au;

up to about 10% In;

up to about 10% Ga;

up to about 10% Sn;

up to about 10% Ge;

up to about 10% Zn;

up to about 10% Mn;

wherein one or more of In, Ga, Sn, Ge, Zn and Mn is present in the amount of about 3 to about 10%;

up to about 1% Ir;

up to about 3% Ru;

up to about 3% Rh; and

up to about 1% Re;

wherein one or more of Ir, Ru, Rh, and Re is present is the amount from about 0.1 to about 3%.

7. The dental alloy of claim 1 further comprising in weight percent:

up to about 0.25% Ti;

up to about 0.25% Al;

up to about 0.25% Si;

up to about 0.25% Hf;

up to about 0.25% B; and

up to about 0.25% Ca;

wherein one or more of Ti, Al, Si, Hf, B and Ca is present in an amount up to about 1%.

8. The dental alloy of claim 6 having a coefficient of thermal expansion from 25° to 500° C. in the range of 8 to $18 \times 10^{-6}/^{\circ}\text{C}$.

9. The dental alloy of claim 6 having a melting temperature in the range from about 1000 to about 1500° C.

10. A dental restoration comprising:

the alloy of claim 6; and

a low-melting dental ceramic having a coefficient of thermal expansion in the range from 25° to 500° C. in the range of 6 to $16 \times 10^{-6}/^{\circ}\text{C}$.

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