

[54] **PALLADIUM ALLOY FOR CERAMIC BONDING**

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[58] **Field of Search** **75/172 R, 134 N, 134 F, 75/170; 32/8**

[56] **References Cited**

UNITED STATES PATENTS

1,999,865	4/1935	Capillon et al.	75/172 R
2,182,041	12/1939	Szabo	75/171
2,226,079	12/1940	Spanner	75/172 R
3,689,254	9/1972	Inove et al.	75/172 R
3,819,366	6/1974	Katz	75/172 R

FOREIGN PATENTS OR APPLICATIONS

1,269,389	7/1961	France	75/172 R
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[57] **ABSTRACT**

A dental casting alloy contains 40–60 percent of a precious metal component which is either palladium alone or a mixture of palladium with platinum in which the platinum is in the amount of up to 12 percent but not in excess of 25 percent of the palladium content. The principal non-precious metal component is 20–50 percent cobalt or is 20–59 percent of a mixture of cobalt and nickel wherein the nickel is in the range of up to 25 percent and not in excess of the cobalt content. An essential modifier is provided by 1–8 percent indium, 1–3 percent tin or 1–8 percent of a mixture of tin and indium wherein the tin does not exceed 3 percent. The alloy may contain as optional additives up to 5 percent zinc, up to 5 percent iron, up to 5 percent tungsten, up to 2 percent ruthenium, up to 2 percent rhodium and up to 10 percent molybdenum. The alloys have a thermal coefficient of expansion of $14.5\text{--}15.2 \times 10^{-6}$ percent per degree Centigrade up to 600° Centigrade. A tooth structure employs a base cast from the alloy upon which is firmly bonded a ceramic coating.

12 Claims, No Drawings

PALLADIUM ALLOY FOR CERAMIC BONDING

BACKGROUND OF THE INVENTION

Dental casting alloys have long been utilized to provide durable, relatively inert base structures upon which there may be fired ceramic compositions to simulate dental enamel. Platinum and gold alloys have been preferred because of their desirable properties during casting and hardening, and various ceramic systems have been developed for use in conjunction with such gold and platinum alloys to provide the desired enamel-like appearance upon such artificial tooth structures.

As a result of the ever increasing price of gold and platinum, there has been an increasing demand for dental alloys of lesser price but affording comparable casting facility and providing equivalent or superior bonding of the ceramic coating. Obviously, such alloys must be relatively inert in the patient's mouth and must have thermal coefficients of expansion closely approximating those of the ceramic materials bonded thereto.

Illustrative of efforts to provide dental alloys relatively low in gold and platinum content are Maulen U.S. Pat. No. 1,807,068 granted May 26, 1931; Bayes U.S. Pat. No. 1,930,119 granted Oct. 10, 1933; Aderer U.S. Pat. No. 1,965,033 granted July 31, 1934; Capillon U.S. Pat. No. 1,999,865 granted Apr. 30, 1935; Spanner U.S. Pat. No. 2,226,079 granted Dec. 24, 1940; and Dietz U.S. Pat. No. 2,310,732 granted Feb. 9, 1943. Other patents of interest from the standpoint of dental alloys employing palladium as a substantial component are Wise U.S. Pat. No. 1,913,423 granted June 13, 1933; Wise U.S. Pat. No. 2,050,077 granted Aug. 4, 1936; and Katz U.S. Pat. No. 3,667,936 granted June 6, 1972. Indicative of an effort to provide a dental alloy having a coefficient of thermal expansion approximating that of porcelain is Hirschhorn U.S. Pat. No. 3,679,402 granted July 25, 1972. Alloys containing substantial amounts of palladium have been employed for various industrial products; illustrative of such alloys are Spanner et al. U.S. Pat. No. 2,222,544 granted Nov. 19, 1940; Rhodes et al. U.S. Pat. No. 2,815,282 granted Dec. 3, 1957; Rhys U.S. Pat. No. 3,085,320 granted Apr. 16, 1963; and Savage U.S. Pat. No. 3,597,194 granted Aug. 3, 1971. Thus, it can be seen that there have been substantial efforts to develop either dental alloys as a substitute for platinum conventionally employed as the precious metal base therein or to develop palladium base alloys for various industrial and dental purposes.

Nevertheless, there has remained a significant need for a relatively low cost dental alloy inert to conditions prevailing in the patients's mouth and to which commercially available porcelain enamels may be readily bonded. To be effective as a dental casting alloy, it is essential that the alloy exhibit a thermal coefficient of expansion within the range of $14.5-15.2 \times 10^{-6}$ percent per degree Centigrade up to 600° Centigrade and that it exhibit casting characteristics similar to those commonly employed in the dental laboratory with high gold and high platinum alloys. Moreover, the alloy must be one which can be processed readily and which will ensure a high strength bond with the ceramic material fired thereagainst in the fabrication of the final tooth structure.

It is an object of the present invention to provide a novel dental alloy inert to conditions in the patients's

mouth and containing not more than 60 percent by weight of platinum group metals.

It is also an object to provide such a dental alloy which is compatible with commercially available porcelain materials and which may be readily cast and processed using techniques similar to those employed in the casting of high gold and platinum content casting alloys.

A further object is to provide such an alloy which will bond firmly and readily to the ceramic coatings fused thereagainst and which will demonstrate a coefficient of thermal expansion closely approximating that of the ceramic material being fired thereagainst.

Still another object is to provide a tooth structure comprising a casting of the novel metal alloy and a ceramic coating firmly bonded thereto.

SUMMARY OF THE INVENTION

It has now been found that the foregoing and related objects may be attained in a dental casting alloy consisting essentially of about 40-60 percent of a precious metal component selected from the group consisting of palladium and mixtures of palladium and platinum wherein the platinum is in the amount of up to 12 percent of the alloy but not in excess of 25 percent of the palladium content. There is included 20-59 percent of a non-precious metal component selected from the group consisting of 20-50 percent cobalt and mixtures of 20-50 percent cobalt and up to 25 percent nickel wherein the nickel content does not exceed the cobalt content. The last essential component comprises 1-8 percent of a modifier selected from the group consisting of 1-8 percent indium, 1-3 percent tin and 1-8 percent of mixtures of tin and indium wherein the tin does not exceed 3 percent. The alloy may contain as optional additives 0-5 percent zinc, 0-5 percent iron, 0-5 percent tungsten, 0-2 percent ruthenium, 0-2 percent rhodium and 0-10 percent molybdenum. The several components of the alloy are balanced to provide a thermal coefficient of expansion of $14.5-15.2 \times 10^{-6}$ percent per degree Centigrade up to 600° Centigrade.

The preferred modifier comprises indium in the amount of 2-5 percent and the preferred alloys contain 45-60 percent of the precious metal component and 35-48 percent of the non-precious metal component. Molybdenum in the amount of 2-8 percent is a desirable additive and nickel in the amount of 10-20 percent desirably comprises a portion of the non-precious metal component.

The aforementioned alloy is cast to provide a base upon which there is firmly bonded a ceramic coating comprised of a glass matrix constituent having a basis selected from the group consisting of feldspar and nepheline and a crystalline constituent of leucite. The ceramic coating is fired against the cast alloy base and is bonded thereto by chemical and diffusion bonding.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

As indicated hereinbefore, the essential components of the alloy constitute palladium or palladium and platinum; cobalt or cobalt and nickel; and a modifier comprising indium, tin or mixtures of tin and indium. The optional additives all provide varying degrees of beneficial properties to the alloy, and obviously other alloying elements may be included although with no presently ascertainable benefit and in some instances deleterious

effects.

More particularly, the precious metal component comprises 40–60 percent by weight of the total alloy and preferably 45–60 percent thereof. Although palladium has been found advantageous as the sole constituent of the precious metal component, it may be used in admixture with platinum wherein the platinum ranges up to 12 percent by weight of the alloy but is not in excess of 25 percent of the weight of palladium in the alloy. When utilizing a mixture of the two metals, the palladium preferably comprises 42–52 percent by weight of the alloy and platinum comprises 3–12 percent by weight of the alloy.

Although cobalt alone may provide the non-precious metal component, the preferred composition utilizes the mixtures of cobalt and nickel. Generally, the non-precious metal component comprises 20–59 percent by weight of the alloy but will only comprise a maximum of 50 percent when the sole constituent is cobalt. In using mixtures of cobalt and nickel, the cobalt content will comprise 20–50 percent of the alloy and the nickel may be present in an amount of up to 25 percent by weight of the alloy but not in excess of the weight percentage of cobalt. Preferably, these mixtures comprise 22–35 percent cobalt and 10–20 percent nickel based upon the weight of the alloy. Within the range set forth above for the non-precious metal component, the tendency for blue cobalt oxide to form and migrate to the surface and discolor the porcelain enamel can be substantially eliminated so that a desirable white alloy is obtained. The nickel tends to widen the melting range and to improve thermal expansion.

The third essential component is the modifier, provided by 1–8 percent indium alone, 1–3 percent tin alone or 1–8 percent of mixtures of tin and indium wherein the tin does not exceed 3 percent by weight of the alloy. Of these possible constituents, indium alone has proven most advantageous with mixtures of indium and tin providing somewhat less advantageous. When used in combination, the indium preferably comprises 2–5 percent of the alloy and the tin comprises 1–2 percent of the alloy. The modifying constituent promotes fluidity of the alloy, lowers its melting range, increases thermal expansion and also serves to deoxidize the alloy. It is believed that the hardening mechanism for the indium-containing alloy is provided by an intermetallic compound of palladium and indium. Moreover, the indium constituent has proven extremely advantageous in promoting optimum bonding of the ceramic coating to the alloy, possibly due to diffusion of indium oxide.

Of the various optional additives, molybdenum in an amount of up to 10 percent has proven beneficial and contributes materially to strengthening of the alloy. When employed, it is preferably utilized in the range 2–8 percent.

Zinc is an optional alloying element in an amount of up to 5 percent and serves as a deoxidizer. When utilized, it is preferably within the range of 1–3 percent.

Ruthenium and rhodium are other optional noble metal alloying constituents and may each be present in amounts of up to 2 percent by weight of the alloy. They tend to provide increased hardness by forming intermetallic compounds with the cobalt although equivalent benefit is substantially obtainable by proper balance of the cobalt/palladium content.

Iron and tungsten in amounts of up to 5 percent by weight of the alloy may be beneficially employed to

improve hardness. The iron is also useful in improving the chemical bonding with porcelain coatings.

As indicated hereinbefore, other elements may be added in small proportions, if they would not materially affect the properties of the alloy. Copper, silver and chromium generally adversely affect the alloy properties.

The following is a specific example of a preferred composition of the present invention,

Element	Percent by weight
Palladium	50
Cobalt	28
Nickel	14
Indium	3
Molybdenum	5

It has been found that the alloys of the present invention will provide a thermal coefficient of expansion of $14.5\text{--}15.2 \times 10^{-6}$ percent per degree Centigrade up to 600° Centigrade and the preferred alloys will provide a thermal coefficient of expansion of $14.7\text{--}15.0 \times 10^{-6}$. Thus, the alloys of the present invention are extremely useful for casting metal substrates to which commercially available porcelain enamels may be bonded by conventional firing techniques. The alloys may be cast at temperatures in the range of about $1285^{\circ}\text{--}1370^{\circ}$ Centigrade and the ceramic coatings may be fired thereagainst at temperatures within the range of $900^{\circ}\text{--}985^{\circ}$ Centigrade. Shear tests of ceramic coatings upon alloy castings indicate extremely high strength bonding provided by both chemical and diffusion bonding with shear strength of 1060 kilograms per square centimeter and even above being readily attained.

In tests, the alloys of the present invention have been found to provide high strength bonding with the conventional feldspar base dental ceramic compositions most widely employed as well as with nepheline syenite base compositions which have been proposed as substitutes therefore. In both such systems, the resultant ceramic coating comprises a glass matrix constituent having a basis which is either feldspar or nepheline and a crystalline constituent of leucite. Although there is apparent diffusion bonding of the coating to the alloy substrate, the alloy substrate does not discolor the ceramic coating and thus conventional color matching techniques may be employed.

During the firing the alloy castings will develop a blue or steel gray coating depending upon the conditions of firing. Use of reduced pressures will favor the formation of blue oxide coatings whereas firing at normal atmospheric pressure favors the formation of a steel gray coating. Proper firing techniques with the alloys of the present invention, however, will not develop coatings which discolor the porcelains fired thereagainst.

The preferred firing techniques involve an initial firing of the casting to a temperature of about $980^{\circ}\text{--}990^{\circ}$ Centigrade, which develops a blue oxide coating. The casting is then pickled in a 50 percent by volume solution of hydrochloric acid and water to remove the blue cobalt oxide. The ceramic coating compositions are then fired against the surface thereof at normal atmospheric conditions. With the preferred compositions, a steel gray oxide coating will develop under the ceramic coating and this does not discolor the ceramic coating. The exposed surfaces of the casting may be pickled and polished to a desired white alloy

appearance.

Illustrative of the efficacy of the present invention are the following specific examples wherein all parts are parts by weight unless otherwise indicated.

EXAMPLE ONE

An alloy is formulated containing 50 percent palladium, 28 percent cobalt, 14 percent nickel, 3 percent indium and 5 percent molybdenum. The thermal expansion of the alloy is found to be 14.8×10^{-6} percent per degree Centigrade. The melting range is observed at 1185°–1260° Centigrade and the alloy is readily cast at a temperature of 1315°–1370° Centigrade.

The physical properties of the alloy are determined by specimens which are heated to 1010° Centigrade and air cooled slowly from 982° Centigrade to 650° Centigrade. The ultimate tensile strength is determined to be 5005 kilograms per square centimeter and the proportional limit is determined at 2706 kilograms per square centimeter with 0.2 percent yield being determined as 3620 kilograms per square centimeter. Elongation of a 2.5 centimeter gage length is found to be 4.6 percent. As cast, the alloy has a Brinell hardness of 176.

This alloy is cast into rods against which is fired a commercially available dental porcelain using a feldspar base. The opaque material fired directly against the cast structure is of the feldspar type of composition described in Wagner U.S. Pat. No. 3,413,723 and has the following nominal oxide analysis:

Oxide	Percent by weight
Silicon dioxide	54
Aluminum oxide	19
Titanium oxide	2
Calcium oxide	1
Potassium oxide	10
Sodium oxide	7
Zirconium oxide	1
Tin dioxide	5
Boron trioxide	1

The translucent coating fired thereupon is again feldspar based and has the following nominal oxide analysis:

Oxide	Percent by weight
Silicon dioxide	61
Aluminum Oxide	20
Potassium oxide	10
Sodium oxide	7
Calcium oxide	2

Firing of the porcelain deposit is conducted at 955° Centigrade at atmospheric pressure to form a ring about the rod. The bond between the ring and the rod is then subjected to shear testing and a shear strength of 1220 kilograms per square centimeter is observed.

The alloy as cast is found to exhibit a steel gray coloration and is pickled with hydrochloric acid and polished to a white coloration approximating that of high platinum alloys. The steel gray oxide coating under the ceramic deposit does not show through the ceramic coating and is highly tenacious.

EXAMPLE TWO

Onto a casting of the alloy of Example One is fired a ceramic coating having essentially the same oxide anal-

ysis as indicated with respect to Example One but using nepheline syenite as the base. The shear strength of the bond between the porcelain coating and the test rod is determined at 1035 kilograms per square centimeter. There is no discoloration of the coating observed in the fired structures.

EXAMPLE THREE

A series of alloy formulations are prepared each containing 50 percent palladium and 5 percent molybdenum. One alloy formulation contains 44 percent cobalt and 1 percent indium. A second alloy formulation contains 43 percent cobalt and 2 percent indium. The third formulation contains 42 percent cobalt and 3 percent indium. The thermal coefficient of expansion of the alloy is found to decrease with an increasing indium content from 15.1×10^{-6} percent per degree Centigrade for the alloy containing 1 percent indium of 14.7×10^{-6} percent per degree Centigrade for the alloy containing 3 percent indium. Increasing the indium content increases the Brinell hardness in the as cast condition from 175 for the 3 percent indium alloy to 190 for the 3 percent indium alloy. All alloy formulations melt well.

When a porcelain composition of the type set forth in Example One is fired thereagainst, a blue oxide layer forms upon the exposed surface of the casting and underneath the ceramic coating. However, it does not show through the ceramic coating and it is tenacious.

EXAMPLE FOUR

An alloy formulation is prepared containing 50 percent palladium, 35 percent cobalt, 7 percent nickel, 5 percent molybdenum and 3 percent indium. The thermal coefficient of expansion of this alloy is found to be 15.0×10^{-6} percent per degree Centigrade and the Brinell hardness as cast is determined at 148. When a ceramic formulation is fired thereagainst, the bond exhibits good shear strength. There is a blue oxide formed on the exposed surface of the alloy casting and under the porcelain deposit, but it does not show through the porcelain coating.

EXAMPLE FIVE

An alloy formulation is prepared containing 59.2 percent palladium, 37.9 percent cobalt and 2.9 percent tin. This formulation is cast at 1205° Centigrade and is found to have a thermal coefficient of expansion of 16.0×10^{-6} percent per degree Centigrade and a Brinell hardness as cast of 180.

When a ceramic coating is fired thereagainst, it is found to exhibit considerably lesser bond strength than that of Example One and the blue oxide coating upon the alloy casting is more intense than observed in Example Three, although it does not show through the porcelain coating.

EXAMPLE SIX

Another test formulation is prepared containing 50 percent palladium, 45 percent cobalt and 5 percent molybdenum. The thermal coefficient of expansion is determined to be 14.7×10^{-6} percent per degree Centigrade and the Brinell hardness as cast is 142. Upon firing of a porcelain coating thereupon, a blue oxide deposit develops upon the exposed surfaces of the casting and underneath the porcelain deposit. This blue oxide coating is found to be loose and flaky and the porcelain coating is chipped off as sheets, indicating

very poor bonding between the porcelain coating and the substrate.

Thus it can be seen from the foregoing examples and detailed specification that the alloys of the present invention provide a relatively low cost dental casting alloy having desirable properties of thermal expansion and inertness to conditions prevalent in the mouth of the patient so as to make them highly suitable for the fabrication of artificial tooth structures. Commercially available porcelains may be fired thereagainst to provide coatings which are tenacious and unaffected by the oxide coating formed upon the casting. The exposed surfaces of the casting may be readily pickled and polished to a desirable white appearance.

Having thus described the invention, I claim:

1. A dental casting alloy consisting essentially of about 40–60 percent precious metal component selected from the group consisting of palladium and mixtures of palladium and platinum wherein the platinum is in the amount of up to 12 percent of the alloy but not in excess of 25 percent of the palladium content; 20–59 percent non-precious metal component selected from the group consisting of 20–50 percent cobalt and mixtures of 20–50 percent cobalt and up to 25 percent nickel wherein the nickel content does not exceed the cobalt content; and a modifier selected from group consisting of 1–8 percent indium, 1–3 percent tin, and 1–8 percent of mixtures of tin and indium wherein the tin does not exceed 3 percent; said alloy containing as optional additives, 0–5 percent zinc, 0–5 percent iron, 0–5 percent tungsten, 0–2 percent ruthenium, 0–2 percent rhodium and 0–10 percent molybdenum, said alloy having a thermal coefficient of expansion of $14.5\text{--}15.2 \times 10^{-6}$ per degree Centigrade up to 600° Centigrade.

2. The dental casting alloy in accordance with claim 1 wherein there is included 1–5 percent zinc.

3. The dental casting alloy in accordance with claim 1 wherein there is included 2–8 percent molybdenum.

4. The dental casting alloy in accordance with claim 1 wherein the non-precious metal component is 10–20 percent nickel and 22–35 percent cobalt.

5. The dental casting alloy in accordance with claim 1 wherein the palladium content is 40–60 percent, the nickel content is 10–20 percent, the modifier is indium in the amount of 2–5 percent, the molybdenum content is 2–8 percent and the cobalt content is 22–35 percent.

6. The dental casting alloy in accordance in claim 1 wherein the modifier is indium in the amount of 2–5 percent.

7. The dental casting alloy in accordance with claim 1 wherein the precious metal component comprises 45–60 percent, the non-precious metal component comprises 35–48 percent and the modifier comprises 2–5 percent.

8. A tooth structure including:

a. a cast base of a metal alloy consisting essentially of about 40–60 percent precious metal component selected from the group consisting of palladium and mixtures of palladium and platinum wherein the platinum is in the amount of up to 12 percent of the alloy but not in excess of 25 percent of the palladium content; 20–59 percent non-precious metal component selected from the group consisting of 20–50 percent cobalt and mixtures of 20–50 percent cobalt and 0–25 percent nickel wherein the nickel content does not exceed the cobalt content; and a modifier selected from the group consisting of 1–8 percent indium, 1–3 percent tin, and 1–8 percent of mixtures of tin and indium wherein the tin does not exceed 3 percent; said alloy containing as optional additives 0–5 percent zinc, 0–5 percent iron, 0–5 percent tungsten, 0–2 percent ruthenium, 0–2 percent rhodium and 0–10 percent molybdenum, said alloy having a thermal coefficient of expansion of $14.5\text{--}15.2 \times 10^{-6}$ per degree Centigrade up to 600° Centigrade;

b. a ceramic coating on at least a portion of the surface of said cast base, said ceramic coating being comprised of a glass matrix constituent having a base selected from the group consisting of feldspar and nepheline and a crystalline constituent of leucite, said ceramic coating being firmly bonded to said cast base.

9. The tooth structure in accordance with claim 8 wherein said matrix basis is feldspar.

10. The tooth structure in accordance with claim 8 wherein the modifier is indium in the amount of 2–5 percent.

11. The tooth structure in accordance with claim 8 wherein the palladium content is 40–60 percent, the nickel content is 10–20 percent, the modifier is indium in the amount of 2–5 percent, the molybdenum content is 2–8 percent and the cobalt content is 22–35 percent.

12. The tooth structure in accordance with claim 8 wherein said ceramic coating is fired against said cast base and is bonded thereto by chemical and diffusion bonding.

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