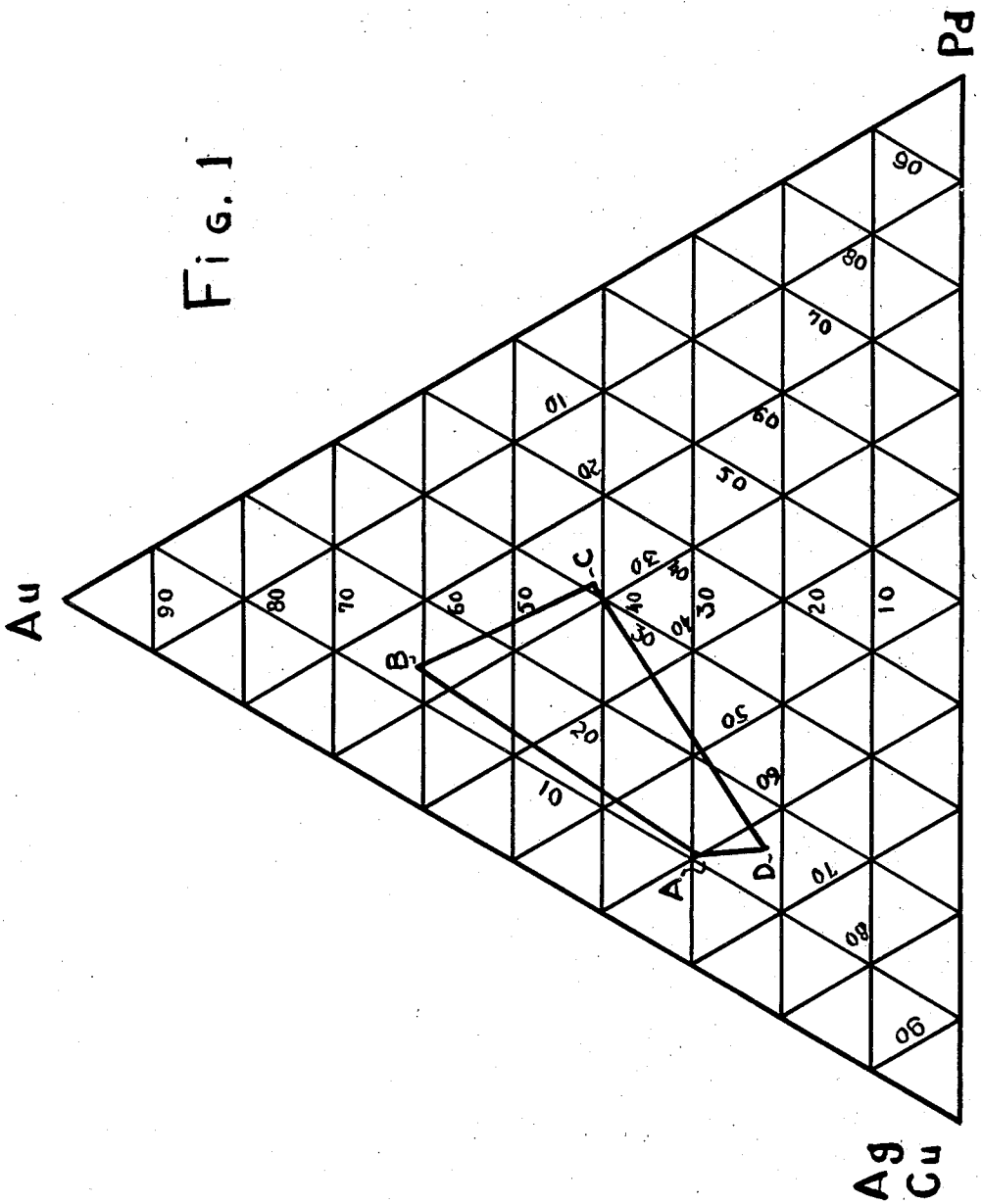
Aug. 4, 1936. E. M. WISE 2,050,077

PALLADIUM DENTAL ALLOY

Filed Aug. 1, 1934 2 Sheets-Sheet 1

Fig. 1



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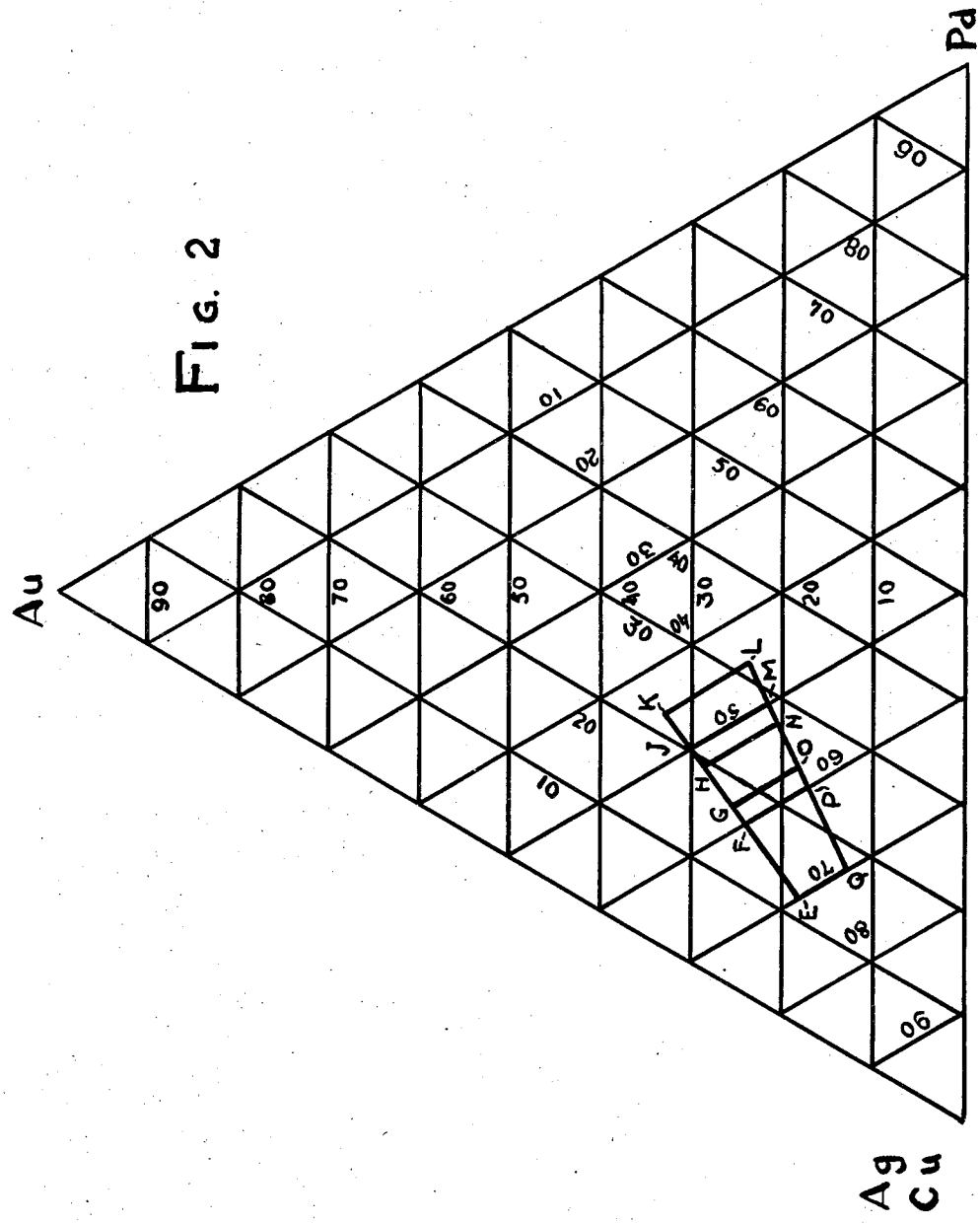
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PALLADIUM DENTAL ALLOY

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FIG. 2



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UNITED STATES PATENT OFFICE

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PALLADIUM DENTAL ALLOY

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Application August 1, 1934, Serial No. 737,896

4 Claims. (Cl. 75—134)

The present invention relates to a palladium dental alloy and more particularly to a dental alloy containing palladium, gold, silver and copper.

Heretofore, precious metal dental alloys which were used for cast or wrought structures contained large percentages of gold, say, about 70% or more by weight in most cases. Frequently, small amounts of silver and copper were added to lower the melting point and to afford a moderate increase in hardness. The harder alloys contained platinum and in some cases lesser quantities of palladium were used in conjunction therewith. The platinum functioned as a hardener and aided in increasing the response to heat treatment while the palladium tended to improve the homogeneity of the alloy and to increase its melting point. It was generally believed that palladium, in contrast with platinum, softened rather than hardened the alloy and reduced its response to heat treatment. Many attempts were made to improve the precious metal dental alloys but proposals made thus far involved certain shortcomings including a deficiency in tarnish and corrosion resistance, a lack of strength and toughness and insufficient cheapness.

As far as I am aware, no palladium dental alloy has been provided which is wholly satisfactory and successful in commercial use and which entirely meets the requirements of the situation.

I have discovered that the prior notions regarding precious metal dental alloys, particularly with respect to palladium, are unsound and I have found that precious metal alloys containing palladium in substantial quantities when used in conjunction with proper proportions of gold, copper and silver have remarkable properties and permit the saving of substantial quantities of gold.

It is an object of the present invention to provide a palladium dental alloy which is strong and tough and which possesses resistance to tarnish, to corrosion and to nitric acid.

A further object of the invention is to provide a palladium dental alloy which can be easily cast and worked and which is responsive to age hardening.

It is also within the contemplation of the present invention to provide a palladium dental alloy which can be made on an industrial scale, which can be handled, fabricated and worked with conventional appliances and equipment, and which is relatively cheap and permits wide use.

Other objects and advantages of the invention will become apparent from the following description taken in conjunction with the accompanying drawings in which:

Fig. 1 is a ternary diagram in which the present palladium dental alloys are plotted on the basis of weight percentages; and—

Fig. 2 is similar to Fig. 1 with the exception that the alloys are plotted on the basis of atomic percentages.

Generally speaking, the present invention contemplates providing a precious metal dental alloy in which the palladium content (expressed in atomic percentage) is not less than 40 nor more than 58% of the combined atomic percentages (26 to 43% of the combined weight percentages) of gold plus palladium, and the palladium content (expressed in atomic percentage) for maximum strength is 50% of the combined atomic percentage (35% of the combined weight percentages) of gold plus palladium. The combined atomic percentage of gold plus palladium may range between 30 and about 55 atomic percent (38.9 and about 73.7 weight percent). When such variations are made the cost and nobility increases with the percentage of gold plus palladium. Increasing the percentage appreciably above 55 atomic per cent (73.7 weight percent), particularly in cast alloys, results in alloys which do not age harden. The strength properties reach a maximum when 22.5 atomic per cent (about 21 weight per cent) palladium and 22.5 atomic per cent (about 39 weight per cent) gold are present, and such an alloy is very suitable for general use where both high strength and corrosion resistance are necessary.

The copper content of the present alloy exerts an important influence upon the hardness as cast or after annealing and upon the age hardening, which can be induced by reheating or slowly cooling the annealed alloy. An alloy containing about 23 atomic percent (19.6 weight percent) palladium, about 29 atomic per cent (45.7 weight percent) gold, about 29 atomic per cent (25.0 weight percent) silver and about 19 atomic per cent (9.7 weight percent) copper developed a

hardness of about 144 Brinell as cast, which was reduced to about 133 when annealed and was increased to 238 when reheated and aged. On increasing the copper content to about 28 atomic per cent (14.7 weight percent) and reducing the silver content a proportionate amount, the alloy developed a hardness of about 169 Brinell when cast, which was reduced to about 159 when annealed and was increased to about 330 when reheated and aged. On further increasing the copper content to about 36 atomic per cent (19.5 weight percent), and reducing the silver content a proportionate amount, the alloy developed a hardness of about 181 Brinell as cast, which was reduced to about 160 when annealed and was increased to about 367 when reheated and aged. Increasing quantities of copper not only lower the melting point, which is perhaps desirable in a casting alloy, but also increase the oxidation during melting. Care should be exercised in adding increased amounts of copper because excessive quantities tends to cause brittleness. The copper content may range between about 16 to 38 atomic per cent (7.84 to 23.68 weight percent) but is preferably held between the limits of 20 to 30 atomic per cent (10.40 to 17.17 weight percent). It has been found that about 25 atomic per cent (about 14 weight percent) is nearly the optimum where high strength and ductility are required.

It is likewise generally desirable to introduce a small amount of a degassifier, such as zinc, to render more easy the production of castings. It should be noted, however, that zinc also hardens the alloy, and if present in excessive amounts, results in undue brittleness. A further disadvantage of excessive quantities of zinc arises from its volatilization during melting, which in turn results in a change in the properties of the alloy. I have also found that the alloys containing excessive quantities of zinc tend to become very hard and brittle when cooled in the mold. For these reasons, I find it best to limit the zinc content to about 3 atomic per cent (about 2.0 weight percent), and in compounding the alloy, to formulate the proportions so that the zinc replaces an equal amount of copper.

Small amounts of deoxidizing or desulphurizing elements may likewise be employed alone or in conjunction with zinc to facilitate the production of sound, ductile castings. Of these, manganese, magnesium, barium, calcium, boron, silicon, and phosphorous, are the most useful. Manganese is the least effective, and likewise exerts the least effect upon the alloy, and may be added in amounts of the order of about 0.2%. Magnesium is powerful and about 0.05 to about 0.1% is about all that can be practically employed. The same rule applies to the last four elements noted. The last three elements are deoxidizers only and must be used with caution to avoid the production of appreciable quantities of low melting phases, which give rise to hot shortness in the alloy. Very small amounts of special elements may be added to refine the grain of the cast alloy. Of these, rhodium and ruthenium in amounts of the order of about 0.1% have been found effective.

Silver constitutes substantially the remainder of the new alloy, aside from minor impurities. The percentage of this metal is determined by the content of the aforementioned constituents to wit: gold, palladium, copper, plus small amounts of such densifying or deoxidizing or grain refining elements as may be present.

The new alloy is responsive to heat treatment and may be softened by heating to about 700–750° C. and quickly cooling. The alloy, after being thus softened, may be hardened by re-heating for 5–15 minutes at a temperature of 350–450° C., or by reheating to 450° C. and then slowly cooling the alloy. An alloy containing 25 atomic per cent (42.3 weight percent) gold, 25 atomic per cent (22.9 weight percent) palladium, 29 atomic percent (15.7 weight percent) copper, 1 atomic percent (0.6 weight percent) zinc, with silver the remainder, showed a tensile strength of 87,000 pounds per square inch, and an elongation of 30% when annealed at 700° C. and quenched, while the same annealed alloy after reheating at 450° C. for 15 minutes showed a tensile strength of 147,000 pounds per square inch, and an elongation of about 8%, whereas slow cooling the alloy from 450° C. resulted in a tensile strength of 139,000 pounds per square inch and an elongation of about 6%. An alloy containing about 20 atomic percent (34.5 weight percent) gold, about 20 atomic percent (18.6 weight percent) palladium, about 25 atomic percent (14.0 weight percent) copper and about 35 atomic percent (32.9 weight percent) silver developed a hardness of about 178 Brinell as cast, which dropped to about 159 when annealed and was increased to about 295 when reheated and aged. A similar alloy containing about 20 atomic percent (34.6 weight percent) gold, about 20 atomic percent (18.7 weight percent) palladium, about 25 atomic percent (14.0 weight percent) copper, about 34 atomic percent (32.2 weight percent) silver and about 1 atomic percent (0.6 weight percent) zinc, developed a hardness of about 304 Brinnel as cast, which was reduced to about 244 when annealed and was increased to about 358 when reheated and aged.

I have likewise discovered that the alloys containing less than 40 atomic percent (about 53.5 weight percent) of gold plus palladium, with copper in the neighborhood of 25 atomic percent (about 14.0 weight percent), exhibit the remarkable and useful characteristic of increasing in hardness when reheated and quenched from temperatures above about 700° C. As an example, the alloy containing 15 atomic percent (27.0 weight percent) gold, 15 atomic percent (14.6 weight percent) palladium, 25 atomic percent (14.5 weight percent) copper, 1 percent (0.6 weight percent) zinc, and silver the remainder develops a hardness of 155 when annealed at 700° C. and quenched, while the hardness is increased to 260 Brinell by quenching from 800 °C.

The liquidus and solidus of the new alloy may be varied over a considerable range, particularly by altering the content of the palladium and copper. Increasing the former raises the melting point, while increasing the latter decreases it. It is important to note that the spread between the liquidus and solidus is moderate, which is not the case with alloys of high platinum content. This small spread and the convenient melting point of the new alloy give rise to maximum castability. The general relation between liquidus and solidus is apparent from the behavior of an alloy containing 25 atomic per cent (22.9 weight per cent) palladium and 25 atomic per cent (42.3 weight per cent) gold with 29 atomic per cent (15.7 weight percent) copper and 1 atomic per cent (0.6 weight per cent) zinc, with silver constituting substantially the remainder, in which the solidus was found to be located at 1000° C., while the liquidus was 1083° C. With the atomic

percentage of palladium equal to that of the gold (weight percentage of palladium equal to 54% of the weight percentage of gold) and with a copper content of 25 atomic per cent (about 14.0 weight per cent), the liquidus will decrease as the amount of gold plus palladium is reduced, and will be 1020° C. with 40 atomic per cent (about 53.5 weight per cent) gold plus palladium, and about 950° C. at 30 atomic per cent (about 42.5 weight per cent) gold plus palladium.

The new alloy, in contrast to alloys of the palladium-silver-copper series, is substantially resistant to nitric acid if the gold content is 15 atomic per cent (about 25.0 weight per cent) or more. This is a matter of great importance as a nitric acid pickle is used by the technicians to remove base metals, etc., from dental castings.

The tarnish resistance of the new alloy has been found to be far in excess of that of a gold-silver-copper alloy containing an equal atomic per cent of gold, while if compared on the basis of equal cost the new alloy shows an even greater superiority.

It is to be observed that the present invention provides an alloy comprising about 16 to about 38 atomic per cent (7.84 to 23.68 weight per cent) of copper, about 30 to about 55 atomic per cent (38.9 to 73.7 weight per cent) of gold plus palladium, the ratio of palladium to the sum of gold and palladium expressed in atomic per cent ranging from 0.40 to 0.58 (or in weight, percentage ranging from 0.26 to 0.43), and silver constituting substantially the balance.

It is also to be noted that the present invention provides an alloy comprising about 20 to about 30 atomic per cent (10.4 to 17.17 weight per cent) of copper, about 42 to about 48 atomic per cent (53.6 to 63.7 weight per cent) of gold plus palladium, the ratio of palladium to the sum of gold and palladium expressed in atomic per cent ranging from 0.45 to 0.55 (or in weight percentage ranging from 0.30 to 0.40), and silver constituting substantially the balance.

Furthermore, the present invention provides an alloy comprising about 25 to about 30 atomic per cent (13.47 to 17.95 weight per cent) of copper, about 30 to about 40 atomic per cent (41.0 to 55.6 weight per cent) of gold plus palladium, the ratio of palladium to the sum of gold and palladium expressed in atomic per cent ranging from 0.40 to 0.55 (or in weight percentage ranging from 0.26 to 0.40), and silver constituting substantially the balance.

The invention further contemplates the provision of an alloy comprising about 20 to about 30 atomic per cent (10.2 to 16.32 weight per cent) of copper, about 50 to about 55 atomic per cent (62.8 to 70.9 weight per cent) of gold plus palladium, the ratio of palladium to the sum of gold and palladium expressed in atomic per cent ranging from 0.45 to 0.55 (or in weight percentage ranging from 0.30 to 0.40), and silver constituting substantially the balance.

Referring more particularly to Fig. 1 of the drawings, it will be noted that the new palladium dental alloys are bounded by the quadrilateral mark A—B—C—D. The approximate percentages of the corners of the quadrilateral expressed in weight percentages of gold, of paladium and of silver plus copper are set forth in the following schedule: The weight percentages of silver and copper are in accordance with the foregoing specification.

Schedule

	A	B	C	D
Au	29.3	60.5	40.9	21.4
Pd	10.6	14.1	30.6	16.0
Ag+Cu	60.1	25.4	28.5	62.6

In Fig. 2, I have plotted the new palladium dental alloys on the basis of atomic percentages. It will be noted that the quadrilateral E—K—L—Q is sub-divided into several smaller quadrilaterals. Thus, the area E—F—P—Q embraces those alloys which are preferably used for casting purposes, although it is to be understood that they may be employed for other uses. The area G—H—N—O embraces those alloys which have high strength and which may be used for cast or wrought purposes. The area J—K—L—M contains those alloys which are especially adapted for wrought purposes while high tarnish resistance is required. The atomic percentages of the various corners of the foregoing quadrilaterals are listed in the following schedule:

Schedule

	E	F	G	H	J	K	L	M	N	O	P	Q
Au	18	24	25.2	28.8	30	33	23.1	21	20.2	17.6	16.8	12.6
Pd	12	16	16.8	19.2	20	22	31.9	29	27.8	24.4	23.2	17.4
Ag + Cu	70	60	58.0	52.0	50	45	45.0	50	52.0	58.0	60.0	70.0

I claim:—

1. An alloy comprising about 7.8 to about 23.7 per cent of copper, about 11 to about 30.6 per cent of palladium, about 22.2 to about 54.2 per cent gold, the ratio of palladium to gold expressed in weight per cent ranging from 0.36:1 to 0.74:1, and silver constituting the balance of the alloy and being present in amount of about 52% to about 6.3%.

2. An alloy comprising about 10.4 to about 17.2% copper, about 16.9 to aout 24.9 per cent of palladium, about 32.3 to about 44.2 per cent of gold, the ratio of palladium to gold expressed in weight per cent ranging from 0.44:1 to 0.66:1, and silver constituting the balance of the alloy.

3. An alloy comprising about 13.8 to about 18.0 per cent copper, about 11.5 to about 21.3 per cent palladium, about 24.7 to about 40.9 per cent gold, the ratio of palladium to gold expressed in weight per cent ranging from 0.36:1 to 0.66:1, and silver constituting the balance of the alloy.

4. An alloy comprising about 10.1 to 16.6 per cent copper, about 19.5 to about 27.7 per cent palladium, about 37.6 to about 49.2 per cent gold, the ratio of palladium to gold expressed in weight per cent ranging from 0.44:1 to 0.66:1, and silver constituting the balance of the alloy.

EDMUND M. WISE.