

July 21, 1936.

O. FEUSSNER ET AL

2,048,648

ALLOY AND PROCESS FOR MAKING SAME

Filed June 19, 1934

Fig. 1.

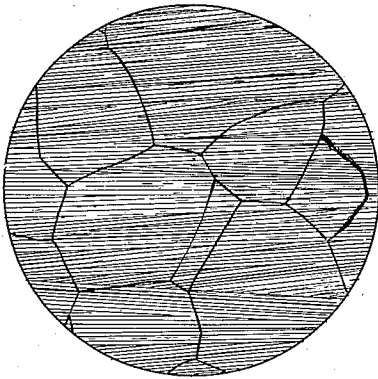


Fig. 2.

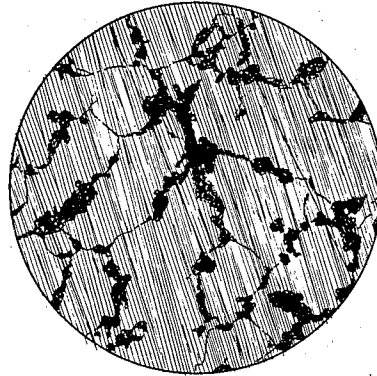


Fig. 3.

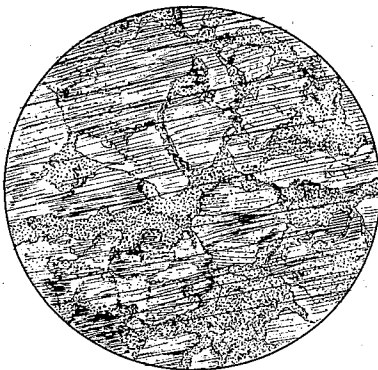
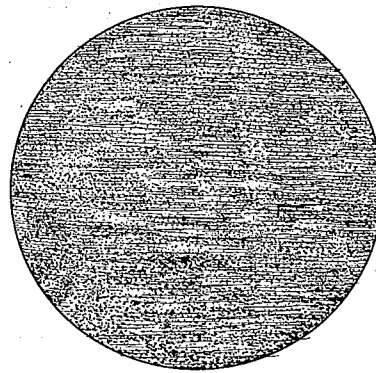


Fig. 4.



BY

INVENTORS
OTTO FEUSSNER
ALFRED JEDELE
Liska & Kellenbeck
ATTORNEYS

UNITED STATES PATENT OFFICE

2,048,648

ALLOY AND PROCESS FOR MAKING SAME

Otto Feussner and Alfred Jedele,
Hanau-on-the-Main, GermanyApplication June 19, 1934, Serial No. 731,258. In
Belgium, France, and the Netherlands July 13,
1932

15 Claims. (Cl. 148—13)

Our present application is a continuation in part of our application Serial No. 622,568 filed in the United States Patent Office July 14, 1932.

Our invention relates to alloys which are intended as substitutes for platinum, for instance in connection with dental work or for making contacts of electrical apparatus etc. The invention consists of novel alloys of the above indicated class having special desirable properties and also consists in a novel method of heat-treating such alloys and thereby improving certain of their properties.

For the purposes indicated above, binary alloys consisting of palladium and silver have been used to some extent. These binary alloys have a greater resistance to corrosion and to tarnish than silver and are also harder than silver. However, even the hardest binary palladium-silver alloy (with equal parts of silver and palladium) has a hardness only about twice the hardness of these two metals, which are very soft. The Brinell hardness of either palladium or silver alone is about 40 kilograms per square millimeter and an alloy made of equal parts of silver and palladium has a Brinell hardness of about 80 kilograms per square millimeter. These binary palladium-silver alloys can not be improved by heat treatment. If a ternary alloy is made by adding gold to the palladium and silver, the resistance to corrosion, to mechanical action and to tarnish becomes very high but heat treatment does not improve these ternary alloys any more than the binary alloys first mentioned. If a ternary alloy is produced by adding copper to palladium and silver, such alloy, which is tarnish-resisting, will indeed show some improvement in hardness when heat treated, but such improvement is only very slight. If instead of copper alone, copper and gold are added to palladium and silver, the resulting alloys are of the same characteristics as the ternary palladium-silver-copper alloys; that is to say, heat treatment, or "aging", will improve their hardness but slightly.

By systematic investigations we have found that considerable improvement is obtained when tin is added in making alloys containing palladium, silver, and another (fourth) constituent which consists either of copper or of gold or of both of these metals. In other words, the new alloys contain at least four metals, three of which are palladium, silver and tin. These new alloys (if their fourth constituent consists of gold alone or of gold with a small proportion of copper) when heated in air do not discolor even at high

temperatures, they are tarnish-resisting and exhibit the surprising property of being improved by heat treatment to such a degree that an increase in hardness of 100% and even more is easily attained. If, in the alloy, the gold is mostly or all substituted by copper, the alloys when heated in air to high temperatures will discolor in a degree increasing with the increase in copper content, but such alloys (containing a relatively large proportion of copper) respond most easily to the process of heat treatment; they show a small initial hardness (natural hardness, soft state) and very great final hardness after the heat treatment, the increase in hardness being quite considerable, exceeding 100% in many cases.

The tin which we incorporate in the above alloys as a special hardener should be used in proportions not less than .5% and not more than 5%. In some cases the metals used as the basis of the alloy may contain small proportions of metals of the platinum group other than palladium, for instance ruthenium, rhodium, or platinum, up to 3%, or up to 3% of these other metals of the platinum group may be added intentionally, without defeating the advantages of the present invention. The presence of these other metals of the platinum group will increase the natural or initial hardness of these alloys and will also increase the final hardness which is obtained by the subsequent heat treatment.

In some cases it is desirable to lower the melting point of the resulting alloys and to increase their liquidity. We have found that when this lowering of the melting point and increase in liquidity are desired, the addition of phosphorus in proportions not less than .5% and not more than 4% will accomplish this result in connection with the above alloys containing tin as a hardener. We have found that the addition of phosphorus (preferably in the form of red phosphorus powder or phosphorus copper) generally decreases the melting point of the alloys by about 150° C. These alloys containing phosphorus have a very low viscosity and flow easily and freely into any cavity. They are especially suitable for casting purposes, for instance in dental work. These phosphorus-containing alloys would be cast in the shape required for the dental work in each particular case. These castings can be adjusted or altered within slight limits, for instance by filing, but can not be hammered or rolled. These phosphorus-containing castings can be improved by heat treatment in the same way as the tin-containing alloys of our inven-

tion containing no phosphorus, and with the same degree of increase in hardness.

The heat treatment of the new alloys is preferably carried out as follows: They are first heated or annealed for a period of not less than fifteen minutes, and preferably from one-half to one hour at temperatures from 700 to 1000° C. and are then quenched in water. The alloys are then in a soft condition, that is to say, they have only their natural hardness. In this condition (if they contain no phosphorus) the alloys can be easily worked and shaped into sheets, wires or any other form that may be desired for the particular use for which they are intended. From this soft condition, the alloys are improved, and particularly increased in hardness, by a heating or aging treatment conducted at temperatures ranging from 400 to 700° C. We have found that the structure of the new alloys is altered considerably during the progress of such heat treatment. When the alloys are in the soft state resulting from annealing at 1000° C. and subsequent quenching, their structure is one with large crystals having very distinct boundaries. If the alloys are then re-annealed or "aged" for a certain length of time, depending on the temperature employed for such aging, deposits or segregations will appear between the crystal boundaries, and it is these deposits or segregations which cause the increase in hardness. The lower this temperature is, the greater will be the length of time required to bring about these segregations; with a temperature of 600° C. about one hour will be sufficient, while with a temperature of 500° C., about three hours will be required to produce these segregations. If the re-annealing or aging is then continued, especially at the relatively high temperature of 650° C., the boundaries of the crystals disappear gradually and have vanished completely after a sufficient lapse of time, say about fourteen hours. The alloys are then of a very homogeneous structure and will exhibit a very minute and uniform grain when pickled. The higher the temperature that is employed, (the more closely it approaches 700° C.) the shorter will be the time required to effect the homogenization of the alloy. It is well known that the size of the grain boundaries determines to a large extent the mechanical properties of any alloy; alloys with large grains are mechanically weaker than alloys with very minute grains. A heat treatment of an alloy which diminishes the size of the grains to the extent indicated above therefore transforms the alloy into a very valuable condition. We desire it to be understood, however, that even a relatively short aging treatment (say of one hour) will increase the hardness of the alloys considerably, but ductility of the alloys (as measured by resistance to repeated bending) is not fully developed by such short treatment. In all cases where a very even and smooth grain is required, the longer heat treatment as referred to above will be employed to produce a very homogeneous hard product of increased ductility.

The preferred proportions employed by us are as follows:

	Per cent
Copper and/or gold.....	5 to 10
Palladium.....	20 to 50
Silver.....	72 to 30
Tin.....	5 to 5

When greater liquidity and the lowering of the melting point are desired as explained above, we

add to the above from 5 to 4% of phosphorus.

It will be understood that in addition to the ingredients just mentioned, the alloys may contain small proportions of metals of the platinum group other than palladium, for instance ruthenium, rhodium, or platinum.

The following examples indicate definite proportions which we have found to be particularly suitable in some cases and also set forth the particular heat treatment which we have employed in these cases:

Example 1

An alloy consisting of 40% of palladium, 50% of silver, 6% of gold, 4% of tin was produced by melting these ingredients and cast to sheet bar. The bar was then annealed for one hour at 1000° C. and quenched in water thereby bringing it into the soft state. The bar was then rolled into a sheet of a thickness of 0.3 millimeters. The rolling operation was generally conducted in a number of successive passes, and between each two passes the metal was subjected to an intermediate annealing at 1000° C. and quenched in water before the next rolling pass. After completion of the rolling operation the sheet was again annealed at 1000° C. and then quenched in water. The metal was then in a relatively soft state, as indicated by the fact that a strip of such sheet would break after being bent 5000 times. Thereupon this soft sheet was aged for fourteen hours at 650° C., and its ductility and other properties were so much improved by this aging treatment that it sustained 15000 bendings before breaking.

Example 2

A series of alloys were prepared each containing 2% of gold and 3% of tin, with the percentage of copper varying from 4 to 7%, that of palladium from 20 to 40% and that of silver from 71 to 48%. Any one of these alloys was treated as follows: It was first annealed at 1000° C. for one-half hour and quenched in water, which treatment brought the metal into the soft condition at which the Brinell hardness amounted to from 100 to 145 kilograms per square millimeter as indicated in Table I below. Then followed a re-annealing or aging for one hour at 600° C. followed by slow cooling whereby the hardness of the alloy in the aged condition was increased considerably, ranging from 180 to 275 kilograms per square millimeter as likewise indicated in the following table:

Table I

Cu	Pd	Ag	Soft	Aged
			Kilograms per square millimeter	
Percent	Percent	Percent		
4	20	71	100	180
5	20	70	110	200
5	30	60	145	225
5	40	50	120	240
6	40	49	120	240
7	40	48	130	275

The increase in hardness produced by the aging treatment of our invention is observed even when the palladium content is more than 40%, but is relatively small in such cases. For instance, when the alloy (with 2% gold and 3% tin) contains 5% of copper, 50% of palladium and 40% of silver, it has a Brinell hardness of 120 kilograms per square millimeter after the annealing treatment at 75

1000° C. for one-half hour followed by quenching in water (soft state), which hardness is increased to 135 kilograms per square millimeter by the aging treatment described above (annealing for one hour at 600° C. and slow cooling).

We may decrease the copper content to 3% in the case of alloys containing 2% of gold and 3% tin. In such cases, however, the increase in hardness obtained by the aging treatment is considerable only when the palladium content of the alloy ranges from 30 to 40%; at palladium percentages below 30 and above 40, the increase in hardness obtained by the aging treatment is relatively slight as will be seen by the following table:

Table II

Cu	Pd	Ag	Soft	Aged
			Kilograms per square millimeter	
Percent	Percent	Percent		
3	20	72	95	120
3	30	62	125	180
3	40	52	110	180
3	50	42	115	120

It will be understood that the annealing treatment and the subsequent aging treatment in connection with alloys of Table II may be the same as described in connection with the alloys of Table I, that is to say, annealing at 1000° C. for one-half hour followed by quenching in water and re-annealing or aging for one hour at 600° C. followed by slow cooling.

The addition of phosphorus in the proportion indicated (from .5 to 4%) is made to any one of the alloys specified above whenever it is desired to reduce the melting point and the viscosity of the alloy while increasing its hardness beyond its natural hardness. The annealing, quenching and aging treatment may be exactly the same for a particular alloy whether or not phosphorus is added thereto. That is to say, if the alloy set forth in Example 1 is changed by simply adding phosphorus thereto within the range indicated, the treatment of such alloy would be exactly the same as described in connection with Example 1. The same remark will apply to the other examples. The addition of phosphorus lowers the melting point of the alloy very considerably and brings it down to the level of the melting point of gold or of gold alloys; this is a considerable advantage in certain cases, particularly for dentists.

The considerable and advantageous alterations in the structure of the material which the heat treatment according to our invention produces, are shown very clearly in the accompanying drawings which are reproductions of microphotographs taken from an alloy of the composition of Example 1 treated according to our invention. These microphotographs were taken with an enlargement of 135 diameters. Fig. 1 shows the structure after annealing for one hour at 1000° C. and quenching; Fig. 2 shows the same alloy after re-annealing or aging at 600° C. for one hour; Fig. 3 shows the condition of the alloy after an aging treatment of seven hours at the temperature of 650° C., (instead of one hour at 600° C.) and Fig. 4 shows the same alloy after an aging treatment of fourteen hours at 650° C.

Where in the appended claims we use the expression "substantially consisting of about", we desire this to be interpreted as meaning that the alloys may also contain other metals of the plat-

inum group in minor amounts, and such substances, as for instance phosphorus, which do not materially change the properties of the alloys to be hardened by heat treatment, but do improve the alloys as to their natural hardness, melting point, liquidity, etc. Again, where in the appended claims we use the expression "from 5 to 10% of a constituent selected from the group consisting of gold and copper", we desire this to be interpreted in accordance with our specification, where we have stated that the preferred proportions employed by us include 5 to 10% of copper and/or gold; in other words, this 5 to 10% constituent may consist either of copper alone, or of gold alone, or of copper and gold together.

Various modifications may be made without departing from the nature of our invention as defined in the appended claims.

We claim:

1. An age hardening alloy substantially consisting of about 20 to 50% of palladium, 72 to 30% of silver, from 5 to 10% of a constituent selected from the group consisting of gold and copper, and 0.5 to 5% of tin.

2. An age hardening alloy substantially consisting of about 20 to 40% of palladium, 71 to 48% of silver, 2% of gold, 4 to 7% of copper, and 3% of tin.

3. An age hardening alloy substantially consisting of about 40% of palladium, 48% of silver, 2% of gold, 7% of copper, and 3% of tin.

4. An age hardening alloy substantially consisting of about 20 to 50% of palladium, 72 to 42% of silver, 2% of gold, 3% of copper, and 3% of tin.

5. A dental element in the form of a member cast in the shape required for the dental work in the particular case, said cast member having the character of an alloy set forth in claim 1.

6. A dental element in the form of a member cast in the shape required for the dental work in the particular case, said cast member having the character of an alloy set forth in claim 1, in which the melting point of the liquid alloy is lowered and the liquidity increased by the addition of not less than 0.5% and not more than 4% phosphorus.

7. An alloy hardened by heat treatment and consisting substantially of about 20 to 50% of palladium, 72 to 30% of silver, from 5 to 10% of a constituent selected from the group consisting of gold and copper, and 0.5 to 5% of tin.

8. A dental element in the form of a member cast in the shape required for the dental work in the particular case, said cast member having the character of an alloy set forth in claim 1 and being hardened by heat treatment.

9. A dental element in the form of a member cast in the shape required for the dental work in the particular case, said cast member having the character of an alloy set forth in claim 1, in which the melting point of the liquid alloy is lowered and the liquidity increased by the addition of not less than 0.5% and not more than 4% of phosphorus, said dental element being hardened by heat treatment.

10. The process which consists in subjecting an alloy substantially consisting of about 20 to 50% of palladium, 72 to 30% of silver, from 5 to 10% of a constituent selected from the group consisting of gold and copper, and 0.5 to 5% of tin, to an annealing treatment at a temperature of from 700 to about 1000° C. and then quickly cooling the alloy thus heated, and thereupon aging it by heating to a temperature ranging from about 400 to 700° C.

11. The process which consists in subjecting an alloy substantially consisting of about 20 to 40% of palladium, 71 to 48% of silver, 2% of gold, 4 to 7% of copper, and 3% of tin, to an annealing treatment at a temperature of from 700 to about 1000° C. and then quickly cooling the alloy thus heated, and thereupon aging it by heating to a temperature ranging from about 400 to 700° C.

12. The process which consists in subjecting an alloy substantially consisting of about 40% of palladium, 48% of silver, 2% of gold, 7% of copper, 3% of tin, to an annealing treatment at a temperature of from 700 to about 1000° C. and then quickly cooling the alloy thus heated, and thereupon aging it by heating to a temperature ranging from about 400 to 700° C.

13. The process which consists in subjecting an alloy substantially consisting of about 20 to 50% of palladium, 72 to 42% of silver, 2% of gold, 3% of copper, and 3% of tin, to an annealing treatment at a temperature of from 700 to about 1000° C. and then quickly cooling the alloy thus heated, and thereupon aging it by heating to a temperature ranging from about 400 to 700° C.

14. The process of producing a dental element which consists in producing in the soft state, an

alloy substantially consisting of about 20 to 50% of palladium, 72 to 30% of silver, from 5 to 10% of a constituent selected from the group consisting of gold and copper, and .5 to 5% of tin, casting such alloy in the shape required for the dental work in the particular case, then heating such casting to a temperature within the range of about 700 to 1000° C., quickly cooling the casting, and thereupon aging it by heating to a temperature ranging from about 400 to 700° C.

15. The process of producing a dental element which consists in producing in the soft state, an alloy substantially consisting of about 20 to 50% of palladium, 72 to 30% of silver, from 5 to 10% of a constituent selected from the group consisting of gold and copper, .5 to 5% of tin, and not less than .5 and not more than 4% of phosphorus, casting such alloy in the shape required for the dental work in the particular case, then heating such casting to a temperature within the range of about 700 to 1000° C., quickly cooling the casting, and thereupon aging it by heating to a temperature ranging from about 400 to 700° C.

OTTO FEUSSNER.
ALFRED JEDELE.