

[54] **TARNISH RESISTANT SILVER BASED
DENTAL CASTING ALLOY HAVING
SUPERIOR IMPROVED DUCTILITY AND
WORK HARDENING CHARACTERISTICS**

[75] Inventor: **Clyde E. Ingersoll**, Tonawanda,
N.Y.

[73] Assignee: **Williams Gold Refining Company
Incorporated**, Buffalo, N.Y.

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[58] Field of Search **75/173 R, 172 G, 134 N**

[56] **References Cited**

UNITED STATES PATENTS

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FOREIGN PATENTS OR APPLICATIONS

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Primary Examiner—L. Dewayne Rutledge

Assistant Examiner—E. L. Weise

Attorney, Agent, or Firm—Christel & Bean

[57]

ABSTRACT

An alloy comprising 10–60% Pd, 0.2–10% of at least one member of the group consisting of Cr, Fe, In, Sn and Zn, the balance silver having improved tarnish resistance meeting the Vickers hardness requirements of the American Dental Association Specification 5 for dental castings, which has superior ductility and work hardening characteristics.

6 Claims, No Drawings

TARNISH RESISTANT SILVER BASED DENTAL CASTING ALLOY HAVING SUPERIOR IMPROVED DUCTILITY AND WORK HARDENING CHARACTERISTICS

U.S. Pat. application Ser. No. 494,566, filed of even date by the same inventor, is directed to a related silver based alloy useful in the dental and jewelry arts.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to silver palladium alloys employed in the dental and jewelry arts which are resistant to tarnishing and which have superior ductility and work hardening characteristics and which meet the requirements of the American Dental Association (ADA) Specification 5 for dental castings.

2. Description of the Prior Art

Gold alloys have long been used in the dental arts for restorative appliances. Soft alloys of gold with small amounts of silver and/or copper were used in earlier times for simple one-surface inlays, where the restoration was surrounded by tooth structure. However, for two or three surface inlays or full crowns, soft alloys of 20K or 22K were not strong enough. More complicated alloys were used to meet the strength requirements. Copper was employed as a strengthening ingredient, silver was used to dilute the gold and produce a cheaper alloy, zinc and/or indium was used as an oxygen scavenger. Palladium and platinum were also used for strengthening, color control and corrosion resistance, the palladium also serving to lower the cost.

As the price of gold increased, cobalt and nickel base alloys were introduced for partial denture use. Silver alloys of platinum or palladium were tried but did not prove successful. However, it was difficult to make precision casts for crowns and inlays from cobalt and nickel base alloys and gold alloys continued to be used for these purposes.

Efforts to substitute silver base alloys for gold base alloys continued. U.S. Pat. No. 2,198,400 shows an alloy containing silver, palladium and hardened with copper and including a small percentage of gold, with zinc as a scavenger. However, as U.S. Pat. No. 2,259,668 points out, copper present in large quantities causes brittleness. Since dental alloys are furnished to the dentist or dental laboratory in the form of wrought pieces, they should be workable by rolling. The prior art alloys, which contain copper as a strengthener, work harden very rapidly. Thus, only a small amount of reduction by rolling can be achieved after each strain relief treatment. In addition, brittle alloys are often undesirable from the point of view of dental technique. In many instances, the dentist must burnish crown margins to give better adaption after cementation. Brittle margins are likely to break off during the burnishing operation.

A further problem with silver dental alloys is the ease with which they tarnish. U.S. Pat. No. 2,196,303; 2,196,304 and 2,259,668 state that zinc and cadmium improve the tarnish resistance of the silver alloys shown, all of which contain large percentages of copper.

SUMMARY OF THE INVENTION

The present invention comprises alloys of silver and palladium containing at least one member of the group

of Cr, Fe, In, Sn and Zn having good ductility and work hardening characteristics and improved tarnish resistance.

OBJECTS OF THE INVENTION

An object of the invention is to provide a silver based alloy having an improved tarnish resistance.

Another object of the invention is to provide a silver based alloy having sufficient strength to be employed for dental and jewelry uses.

Another object of the invention is to provide an alloy having sufficient ductility to enable dental constructions formed therefrom to be burnished or adjusted without fracturing.

A further object is to provide a silver based alloy having lowered work hardening characteristics whereby rolling of alloy bars into strips can be accomplished without excessive strain relief heat treatments.

A further object is to provide a silver based alloy having improved tarnish resistance, improved ductility and lessened work hardening characteristics without loss of properties necessary for casting, such as fluidity for filling a mold completely and for polishing.

Yet a further object is to provide a silver based alloy of improved characteristics for dental and jewelry uses comprising:

Element	Broad range, %	Preferred range, %
Pd	10-60	15-30
At least one of the group consisting of Cr, Fe, In, Sn and Zn		
Ag	2-10 Rest	.5-10 Rest

Further objects of the invention will become apparent from the following description and claims.

DESCRIPTION OF THE INVENTION

Specification 5 of the ADA has for many years included four types of casting alloys in common use in dentistry. These Are: Type I, for one surface inlays having 50-90 Vickers hardness; Type II, for $\frac{3}{4}$ crowns, abutments and pontics; Type III, having 120-150 Vickers hardness for thin backings, pontics, full crowns and saddles; and Type IV having 150 minimum Vickers hardness, hardenable to 220 minimum Vickers hardness for partial dentures, bars, clasps and unit castings.

TARNISH RESISTANCE

Publication No. 31,008 of the Department of Commerce dated Sept. 23, 1927 gives the results of tests on the tarnishability of silver-based alloys. According to the publication, the alloys were exposed to sodium polysulfide for a period of 8 minutes and the discoloration noted. In the present case, this test was modified by substituting ammonium sulfide, which was found to give more reproducible results. In the corrosion tests employed, cast bar specimens were prepared by first grinding and polishing by normal metallurgical methods, followed by sand blasting the surface to be exposed to ammonium sulfide for 8 minutes.

A numerical scale was established by exposing pure silver bars to ammonium sulfide for times ranging from 0 to 145 seconds, giving a scale of 0 for no exposure to 10, almost black. In making the test, a portion of the test bar was covered so that the exposed portion and unexposed portion could be directly compared. Dental

amalgam rated 9 on this scale, an alloy of 75 silver-25 palladium rated 5. An ADA certified gold alloy rated between 0 and 1 and was assigned ½. To be acceptable for dental work of the type covered in ADA specification 5, the tarnish rating should be no higher than about 5.5.

HARDENING

Elements in addition to copper may be employed to harden a silver-based alloy containing palladium. A partial list of elements is given in Table I, along with the hardness obtained by adding them to an alloy containing 75% Ag, 25% Pd.

TABLE I

ADDED	PERCENTAGE	VICKERS HARDNESS
ELEMENT	ADDED	
None	—	70
Cobalt	10	120
Cobalt	11	130
Chromium	2½	125
Copper	22	245
Iron	4	127
Germanium	2.2	103
Hafnium	4	104
Indium	4½	160
Manganese	2	95
Molybdenum	1-2	80
Nickel	11	130
Tin	4	200
Tantalum	1.1	95
Titanium	1.6	140
Vanadium	0.1	92
Tungsten	4	87
Zinc	4	163
Zirconium	4	132

Improved sulfide tarnish resistance is given in Table II by the addition of the enumerated elements to a 75% Ag, 25% Pd alloy:

TABLE II

ADDED	PERCENT ADDED	TARNISH RATING
ELEMENT		
None	—	5
Cobalt	to 7%	4
Cobalt	7%	5
Chromium	.2-2.9+	2-5
Copper	4 to 22	3-5
Iron	1-6	2-5
Indium	up to 4%	1-2
Tin	2-7	2-5
Tantalum	.2 to 1.1	3-5
Titanium	.2-1.1	4-5
Tungsten	1 to 74	3-5
Zinc	2-7	2-5

It was found that in the case of some of the elements which in lower concentrations had the effect of improving sulfide tarnish resistance had the opposite effect on higher concentrations. Thus, adding 25% indium to produce an alloy having 135 Vickers rating resulted in unacceptable tarnish number of 7.

It has been discovered that employment in a silver-palladium alloy of certain elements and combinations thereof in specific ranges results in alloys having improved ductility, work hardening characteristics and resistance to tarnishing. These elements are broadly chromium, iron, indium, tin and zinc and, more preferably indium, tin and zinc.

Since hardness is not translatable from one alloy system to another, some other mechanical property must be employed to compare different systems. In the present case, the 0.1% offset yield strength was used as the comparable property. The Vickers hardness shown in the table is for a silver base alloy of this invention having the same 0.1% offset yield strength as the ADA specification 5 Type alloys.

TABLE III

TYPE	0.1% OFFSET YIELD	VICKERS HARDNESS
STRENGTH		
(ADA Specification No. 5)	(Gold or Silver based alloy)	(Silver base alloy)
I	20,000-27,500 psi	85-105
II	27,500-36,000 psi	105-145
III	36,000-44,500 psi	145-200
IV	44,500+	200+

These values are all in the "as cast" condition.

Examples of alloys for Type I (HV 85-105) are listed in Table IV:

TABLE IV

Alloy No.	Ag	Pd	Cr	Fe	In	Sn	Zn	HV	Tarnish	Cold Reduction
1	Bal	23.95	0.7	—	—	—	—	85	3	90%+
2	Bal	23.35	1.1	—	—	—	—	97	3	90%+
3	Bal	23.50	—	1	—	—	—	105	2	90%+
4	Bal	25	—	—	2	—	—	86	2	90%+
5	Bal	25	—	—	3	—	—	99	2	90%+
6	Bal	25	—	—	—	1	—	90	2	90%+
7	Bal	25	—	—	—	—	1	97	2	90%+
8	Bal	24.5	—	.25	.44	.33	.22	95	3	90%+
9	Bal	24.5	—	—	1	1	—	91	5	90%+
10	Bal	24.5	—	—	—	1	1	98	4	90%+
11	Bal	24.5	—	—	1	—	1	90	4	90%+

Examples of alloys for Type II (HV 105-145) are listed in Table V:

TABLE V

Alloy No.	Ag	Pd	Cr	Fe	In	Sn	Zn	HV	Tarnish	Cold Reduction
1	Bal	22.6	1.6	—	—	—	—	120	3	90%+
2	Bal	21.7	2.2	—	—	—	—	120	4	90%+
3	Bal	20.65	2.9	—	—	—	—	126	4	90%
4	Bal	22	—	—2	—	—	—	125	3	90%+
5	Bal	19	—	4	—	—	—	128	4	90%+
6	Bal	25	—	—	3.5	—	—	120	2	90%
7	Bal	25	—	—	—	2	—	140	2	86%
8	Bal	25	—	—	—	—	2	130	2	87%
9	Bal	24.5	—	—	—	—	1	113	3	89%
10	Bal	24	—	.5	—	—	.5	113	3	90%+
11	Bal	24	—	.5	2	—	—	114	3	90%+
12	Bal	24	—	1	1	—	—	135	3	90%
13	Bal	24.25	—	—	2	1	—	140	4.5	90%
14	Bal	24	—	—	3	—	1	130	4	90%+
15	Bal	24	—	—	2	1	1	141	4	89%

Examples of alloys for Table III (HV 145–200) are listed in Table VI:

TABLE VIII-continued

TABLE VI

Alloy No.	Ag	Pd	Cr	Fe	In	Sn	Zn	HV	Tarnish	Cold Reduc.
1	Bal	19	—	6	—	—	—	148	5	70%
2	Bal	25	—	—	4	—	—	150	1	89%
3	Bal	25	—	—	—	6	—	186	4.5	62%
4	Bal	25	—	—	—	—	4	165	4	58%
5	Bal	24.75	—	.25	1.1	.82	.55	162	3	89%
6	Bal	24.50	—	.5	.18	1.08	.72	173	3	80%
7	Bal	24.25	—	.75	—	.9	6	182	3	89%
8	Bal	24	—	1	1.1	.82	.55	191	4	77%
9	Bal	24.25	—	—	1	1	1	150	4.5	89%
10	Bal	24	—	—	1	1	2	160	4	65%
11	Bal	23.75	—	—	2	—	3	175	4.5	51%
12	Bal	23.5	—	—	5	—	1	195	4	58%
13	Bal	23.25	—	—	4	3	—	184	4.5	56%
14	Bal	23	—	—	4	—	4	183	4.5	40%
15	Bal	22.5	—	—	1	4	5	155	5.5	35%

Examples of alloys for Type IV (HV 200+) are listed in Table VII:

RANGES OF ELEMENTS OF THE SILVER BASED ALLOY (PERCENT)

Cr, Fe, In, Sn, Zn .2–10 .5–10

TABLE VII

Alloy No.	Ag	Pd	Cr	Fe	In	Sn	Zn	HV	Tarnish	Cold Reduc.
1	Bal	25	—	—	—	4	—	206	4	86%
2	Bal	24.75	—	.25	1.76	1.32	.88	204	4	64%
3	Bal	23.75	—	—	4	1	—	218	4.5	71%
4	Bal	23.50	—	—	2	3	1	205	4	52%
5	Bal	23.25	—	—	6	1	—	219	4.5	52%
6	Bal	23	—	—	5	2	1	215	4	36%
7	Bal	22.5	—	—	6	4	—	202	4.5	37%

The following are the ranges of elements of the silver based alloy of the present invention:

TABLE VIII

RANGES OF ELEMENTS OF THE SILVER BASED ALLOY (PERCENT)

	Broad	Preferred
Silver	30–89.8	60–84.5
Palladium	10–60	15–30
1 or more of the group of Cr, Fe, In, Zn, Sn		
Type I	2–2.7	.5–2.5
Type II	1.0–4.4	1.5–4.1
Type III	2.0–10	2.6–10
Type IV	4.0–10	6.9–10
OVERALL RANGE FOR ALL TYPES		
Silver	30–89.8	60–84.5
Palladium	10–60	15–30
1 or more of		

50 What is claimed is:

1. An alloy consisting essentially of about 15–30% Pd, about 0.2–10% of an element of the group consisting of Cr, Fe, and In and mixtures thereof and the balance Ag.

55 2. The alloy of claim 1 wherein the content of the element of the group is about 0.5–10% and the balance Ag.

3. The alloy of claim 1 consisting essentially of about 23.5% Pd, about 1% Fe and the balance Ag.

60 4. The alloy of claim 1 consisting essentially of about 25% Pd, about 3.5% In and the balance Ag.

5. The alloy of claim 1 consisting essentially of about 24.25% Pd, about 0.75% Fe, about 0.9% Sn, about 6% Zn and the balance Ag.

65 6. The alloy of claim 1 further including from about 0.2–10% of an element of the group consisting of Sn and Zn and mixtures thereof.

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