

ing detailed description of the preferred embodiments, the appended claims, and the accompanying drawings. As depicted in the attached drawings:

FIG. 1 is a graphical representation of the effect of acid-assisted consolidation on the transverse rupture strength of silver compacts.

FIG. 2 is a graphical representation of the effect of particle size on the transverse rupture strength and density of hand-consolidated compacts.

FIG. 3A is a graphical representation of the agglomerate size distribution of precipitated silver powder using the precipitation formulation of Table 1, Solution A.

FIG. 3B is a graphical representation of the agglomerate size distribution of precipitated silver powder using the precipitation formulation of Table 1, Solution B.

FIG. 4 is a graphical representation of the effect of annealing temperature on the transverse rupture strength and density of hand-consolidated compacts using the precipitation formulation of Table 1, Solution B.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will be disclosed in terms of the currently perceived preferred embodiments thereof

The present invention is based on the ability of silver surfaces to adhere to each other after being treated in dilute acid. Silver particles that have been immersed in dilute acid can be condensed into cohesive solids, and display transverse rupture strength values significantly superior to that attained by pressing untreated powder, as depicted in FIG. 1. The ability to condense surface-treated silver powder into a cohesive solid displaying reasonable mechanical properties, as well as the established and approved use of silver as a dental restorative material, clearly suggests that a silver-based material is a likely candidate for a mercury-free substitute to dental amalgams.

The inventors have developed procedures and powder properties that facilitate the hand consolidation of material having properties which compare favorably to those of conventional dental amalgam. A range of particle sizes has been developed and a pre-consolidation thermal treatment has been established which promotes consolidation but does not adversely affect powder handling. Silver powder of the required particle size is best obtained through the present two solution precipitation process.

While investigating the immersion deposition of silver onto tin in which Ag^+ is reduced by the oxidative dissolution of tin, the inventors observed that Sn^{2+} can be further oxidized to Sn^{4+} , resulting in additional Ag^+ reduction and the precipitation of finely-divided silver. The chemistry most to extensively explored in this study consists of a mixture of a silver salt and a tin salt in a 1.0 mol/l acid solution. The following reactions occur



and yield a metallic silver precipitate with a small particle size and an irregular morphology.

The acid is an inorganic or organic acid and can be selected from the group consisting of fluoroboric acid, acetic acid, perchloric acid, phosphoric acid, sulfamic acid, and sulfuric acid, with fluoroboric acid being preferred. The silver salt can be selected from the group consisting of silver nitrate, silver oxide, silver fluoroborate, silver fluoride,

silver perchlorate, silver sulfamate, and silver sulfate, with silver nitrate being preferred. The tin salt can be selected from the group consisting of tin fluoroborate, tin fluoride, and tin sulfate, with tin fluoroborate being preferred.

In order to ensure the deposition of pure silver, the concentrations of the reactive species and the pH of the solution must be properly adjusted. Too high a tin ion concentration or an inappropriate pH may lead to the formation of tin oxide in the solution and its precipitation and incorporation into the silver. Thermodynamically, it may be possible to have some underpotential deposition of tin where silver-rich, Ag—Sn intermetallics are formed. The free energy associated with the formation of the Ag—Sn intermetallic increases the $\text{Sn}^{2+} \rightarrow \text{Sn}(\text{Ag})$ reduction potential so that this side reaction may, in principle, occur.

Of those properties which best promote hand consolidation, one of the most important parameters is the agglomerate size of the silver powder. As illustrated in FIG. 2, a dramatic increase in both the transverse rupture strength and density of hand consolidated samples can be achieved as the maximum agglomerate size of the silver powder is decreased. A statistically insignificant increase in the rupture strength is observed when the largest agglomerate size is reduced from 25 to 21 μm . These results clearly indicate that an agglomerate size greater than about 40 μm should be avoided.

Further, the precipitation process should be optimized so that an agglomerate particle size of less than 40 μm can be obtained, preferably without sieving. Fractional sieving is time consuming, can damage the silver by introducing workhardening to an otherwise ductile material, and promotes the cold welding of small particles into larger agglomerates. For these reasons there is a lower limit to the maximum agglomerate size one can achieve using progressive sieving.

Typical solution chemistries for silver precipitation are shown in Table 1.

TABLE 1

Solution composition used for the precipitation of silver.		
	Solution A	Solution B
Silver Nitrate	0.433 mol/l	0.433 mol/l
Fluoroboric Acid	1.000 mol/l	1.000 mol/l
Anionic Surfactant	3.9×10^{-5} mol/l	3.9×10^{-5} mol/l
Alumina (γ -0.05 μm)	0.0033 mol/l	0.0033 mol/l
Tin Fluoroborate	0.210 mol/l	0.210 mol/l
Ag/Sn Ratio	2.062	2.062
pH	0.4	0.4
Temperature	21° C.	21° C.
Agitation	Mechanical (Stir Bar)	Mechanical (Stir Bar)
Colloid (Gelatin)	0 ppm	15 ppm

Alumina is added to the precipitation solution to inhibit clumping during precipitation and to retard sintering of powders when heat treated at elevated temperature. A surfactant, such as sodium 2-ethylhexyl sulfate (Niaproof Anionic Surfactant 08), is added to disperse the alumina during powder precipitation and to inhibit clumping of the precipitated powders. The early stages of precipitation produce particles which range in size from 0.2 to 2 μm . By the time these particles are collected, however, they are generally fused into agglomerates which vary significantly in size. These agglomerates are likely formed during the middle to latter stages of precipitation where existing particles act as nucleation sites and promote branching. As depicted in FIG. 3A, the silver powder formed from Solution A has a bimodal distribution of particle sizes, with 62 wt. % of the agglom-