JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE **11** (2000) 469–479

A study of alternative metal particle structures and mixtures for dental amalgams based on mercury additions

J. A. MARQUEZ, L. E. MURR, V. AGÜERO
Department of Metallurgical and Materials Engineering and Materials Research Institute, The University of Texas at El Paso, El Paso, TX 79968–0520, USA

The perception that mercury in dental amalgam is toxic to the human organism has prompted worldwide efforts by the scientific community to develop alternative amalgam-like materials that utilize little or no mercury. In this investigation, an attempt is made to develop a new dental alloy system by adding liquid mercury to silver-coated Ag_4Sn intermetallic particles in lesser amounts than are used in conventional amalgam alloys. An effort to precipitate the important eta-prime (Cu_6Sn_5) phase was made by adding pure Cu and Sn powders to the alloy formulation during trituration. Tytin® a popular Ag-Sn-Cu single-composition, spray-atomized conventional dental alloy was used as the control to obtain baseline data for comparisons of microstructures and mechanical properties. Amalgamation of the coated particles with mercury, with or without the addition of Cu and Sn powders, mostly produced specimens with chemically non-coherent microstructures that were relatively weak in compression. These results were due, in part, to mercury's inability to chemically wet the Ag-coated particles and Cu and Sn powders because of naturally occurring surface oxide films. The strongest specimens tested had silver dendritic coatings, resulting in compression strength values up to 40% of the control's. Their higher strength is attributed to mechanical interlocking at the particle/matrix interfaces.

1. Introduction and background

Silver-tin amalgams are believed to have been first utilized as a filling material during the T'ang Dynasty, c. AD 700, by Chinese physicians [1]. Historical accounts by Craig [2] and Roggenkamp [3] indicate that they were not used in the West until the early 1800s. Amalgam was introduced in England in 1819 and a paste was developed in France in 1826 that contained bismuth, lead and tin. Prior to applying it to the tooth, the alloy was mixed with mercury, melted and then poured into the cavity at about 100 °C, an ordeal that required enormous tolerance and fortitude by the patient! Improvements by other investigators led to a lowering of the condensing temperature through the addition of silver filings to the alloy mixture, a discovery that spared the patient from further dental trauma. The amalgam produced was harsh and difficult to mix, hardened slowly and had large dimensional changes during setting.

With improvements in alloy chemistry and fabrication technology in the late 1800s, amalgams became easier to place and more widely accepted. By adding tin to the mixture during the amalgamation procedure, a more plastic mass was produced that set more rapidly and had better handling characteristics. Silver-tin alloys and their amalgams were investigated scientifically in the late 1800s by J. Foster Flagg, and those studies were continued into the twentieth century by G. V. Black, perhaps the most renowned researcher and clinician in the history of dentistry. Black's studies led to the development of classical standards that have shaped clinical protocol affecting the design of cavity preparations, techniques involved in trituration and condensation of amalgam, as well as surface treatment of the restoration to prolong its clinical life [3].

Silver amalgams were introduced as dental restoratives to the United States around 1833 by the Crawcour brothers, controversial British entrepreneurs who called their product ''Royal Mineral Succedaneum''. They experienced great commercial success but their advertisement claims and questionable use of the new material offended members of the American Society of Dental Surgeons, who declared the use of amalgam by its practitioners as malpractice [4].

Historically, amalgam alloy powders have contained at least 65 wt % silver, 29 wt % tin and less than 6 wt % copper, the composition that closely approximates that recommended by Black in 1896 [5]. During the 1960s and 1970s, new developments were made in the formulation and manufacture of these alloy powders that improved their clinical properties. Copper content was increased from < 6 wt % to 10–30 wt %, resulting in amalgams that had improved marginal integrity, less plastic deformation (creep) and higher corrosion resistance.

Dental alloy powders traditionally have been obtained from lathe-cut chips of cast ingots. Now they can be spray atomized from the liquid phase and quenched in either water or inert gas chambers, producing spherical and oblong particles that have high surface areas and better handling characteristics when mixed with mercury. Admixed amalgams are produced by mixing the lathe-cut filings with silver-copper eutectic particles. Also, spherical particles with a Ag-Sn-Cu ternary chemical formulation presently are manufactured from single composition melts.

In 1963, Innes and Youdelis [6], Canadian dental scientists, made the first major change in the chemical composition of amalgam alloy powders since the original alloy formulation of Black in 1896. They discovered that the creep properties of amalgam could be improved by at least one order of magnitude by increasing the copper content above the traditional 6 wt % in the powder alloy mixture. In their study, they added one part spherical Ag-Cu eutectic particles (72% Ag–28% Cu) to two parts of the conventional lathe-cut Ag–Sn filings, creating an admix high-copper alloy.

Amalgam made from this two-powder combination was found to be stronger than amalgam made from either lathe-cut or spherical low-copper powders. This benefit was due primarily to the reduced plasticity and higher strength imparted by the formation of the eta-prime (η') phase in high-copper mixtures. Admixed alloys usually contain 30–55 wt % spherical high-copper powder particles with the remainder being low-copper lathe-cut filings, and their total copper content ranges from 9–20 wt %.

In 1971 Asgar [7] developed a high copper amalgam alloy from a single cast Ag/Cu/Sn ternary system, in contrast to the blending of two different powders as in the Innes and Youdelis method [6]. The powder mixture of 60 wt % silver, 27 wt % tin and 13 wt % copper was melted, cast, and the single-composition particles were produced as either lathe-cut or spray-atomized spherical. The new product was called high-copper single composition alloy. Although its marginal integrity and corrosion resistance have been excellent, its packing efficiency has not been quite as good as those of admixed alloys. This has prompted alloy manufacturers to continue producing admixed alloys, but with improved formulations.

The use of zinc as part of the formulation for amalgam alloy powders has advantages and disadvantages, at times causing some controversy. Most alloys seldom contain zinc to an extent greater than 1 wt %. It is added by the alloy manufacturer during melting to act as a deoxidizer, to scavenge for oxygen and unite with the other components to form compounds resistant to oxidation. Zinc also imparts more plasticity to the amalgam, making it easier to condense and carve.

In 1986, the International Standards Organization (ISO) adopted a more specific standard for amalgam that sets the chemical composition (in wt %) at a minimum of 40% silver and maximums of 32% tin, 30% copper, 2% zinc and 3% mercury in the alloy powder [8].

Currently, amalgam alloys are sold to the dental practitioner through various supply houses as combinations of either high or low copper, spherical or lathe-cut and single-composition or admixed. Table I summarizes some of the most popular alloys in current use by dentists in the United States, Europe and Japan.

The relative proportions of elements in the amalgam powder alloys are currently regulated in the United States by American Dental Association Specification #1, adopted in 1977. It requires that the chemical composition of the powders contains silver and tin essentially, but allows for the inclusion of copper, zinc, gold and mercury in amounts smaller than the silver or tin content.

1.1. The amalgamation process

The chemical reaction at room temperature between elemental liquid mercury and Ag-Sn-Cu blended alloy particles involves the ''wetting'' by mercury of the particle grain boundaries in the mixture, creating low energy interfaces along which the grains can slide and separate from each other. These grains intermix and continue to react with mercury and other separated grains in the multi-phase matrix to form new phases of intermetallic compounds. The products of the reaction also include unreacted alloy particles that are trapped within the base matrix and become a part of the hardened amalgam structure.

Mixing, or trituration, of the amalgam is accomplished in the modern dental operatory through the use of prefabricated plastic capsules. These are cylindrically-shaped containers that contain dual internal compartments, one containing liquid mercury and the other a powdered mixture of Ag/Sn/Cu particles plus a plastic pestle. The two compartments are separated by a thin plastic membrane that is ruptured by the operator prior to agitating the capsule in a mechanical triturator for 10–15 s.

When the membrane ruptures, mercury enters the powder alloy compartment, where it partially dissolves the metal particles and produces a soft, plastic mass that is removed from the capsule and condensed into a prepared tooth cavity by the dentist. Within a few minutes the amalgam restoration attains its initial set and begins to crystallize and harden through a series of complex chemical reactions. The three major components in amalgam are silver, tin and mercury, with copper added as a fourth component to improve the alloy's resistance to creep. As it turns out, increased copper also alters the phase formation.

A setting expansion, as in admixed alloys, logically is desirable to lock the restoration against the cavity walls, causing slight creep deformation at the margins. Single-composition alloys, however, have demonstrated good clinical performances against undue leakage at the margins despite their ultimate volume contraction. The overall problem of marginal leakage is complicated and likely due to a combination of factors that include the setting expansion and contraction of the alloy, formation of aqueous corrosion products at the interface, plastic deformation (creep) of the alloy from masticatory forces, as well as the occasional presence of a liner material between the tooth and restoration that is in contact with the oral environment.

Most amalgams, when first placed, show marginal leakage to oral fluids when they are subjected to temperature cyling during eating and drinking. The

TABLE I Chemical compositions of some amalgam alloys used in the United States, Japan, and Europe

Type*	Product (trademark)	Chemical composition (wt %)				
		Ag	Sn	Cu	Zn	Other
HCSS	Aristaloy CR	58.7	28.4	12.9	—	—
HCSS	Cavex Avalloy SF	45.0	30.5	24.0	0.5	—
HCB	Cavex nongamma 2	69.2	18.6	11.9	0.3	—
LCS	Cavex SF	72.0	26.0	1.5	0.5	—
HCB	Cupralloy	62.1	15.1	22.7	—	—
HCB	Dispersalloy	69.7	17.7	12.0	0.9	—
HCSL	Epoque 80 (ANA 2000)	43.0	29.0	25.0	0.3	Hg2.7
HCSS	Indiloy	60.6	24.0	12.1	—	In 3.4
LCL	New True Dentalloy	70.9	25.8	2.4	1.0	—
HCSS	Sybraloy	41.2	30.2	28.3	—	—
HCSS	Tytin	59.4	27.8	13.0	—	—

restoration, having a thermal expansion coefficient (25×10^{-6} per °C) more than twice the surrounding tooth structure (11×10^{-6} per °C), expands and contracts more than the tooth during thermal cycling. On cooling, a space forms between the restoration and cavity wall into which saliva percolates, from which it is then expelled when the restoration expands. Formation of amalgam corrosion products effectively seals the interface to present the undesirable effects of saliva percolation. Amalgam is quite unique in this respect, being the only dental restorative material that benefits from the formation of corrosion products [9].

During the process of trituration of traditional lathe-cut alloy powders, silver and tin in the outer surface layers of the low-copper particles dissolve into the mercury. Due to the limited solubility of silver (0.035 wt %) and tin (0.06 wt %) in mercury at room temperature, two kinds of intermetallic compounds, gamma-1 (γ_1) Ag_2Hg_3 (body-centered-cubic) and gamma-2 (γ_2) Sn_8Hg (simple hexagonal) start to precipitate out of the solution according to a dissolution precipitation process. Silver reaches its saturation concentration in mercury before tin, so silver supersaturation results in the precipitation of gamma-1 (γ_1) before the precipitation of gamma-2 (γ_2). The alloy is usually mixed with 40–50 wt % mercury, which is insufficient to consume the alloy particles completely. Unconsumed particles are present, therefore, in the hardened amalgam and are surrounded and bound together by minute, equiaxed gamma-1 grains (1–3 microns in size), and irregularly shaped gamma-2 crystals [2]. The following chemical equation illustrates a typical amalgamation reaction in a traditional low-copper alloy:

$$\begin{aligned} &Ag_3Sn\ \text{(gamma)} + Cu_3Sn\ \text{(epsilon)} \\ &\quad + Hg > Ag_2Hg_3 \quad \text{(gamma-1)} \\ &\quad + Sn_8Hg \quad \text{(gamma-2)} + Ag_3Sn\ \text{(unreacted)} \\ &\quad + Cu_3Sn\ \text{(unreacted epsilon)} \end{aligned}$$

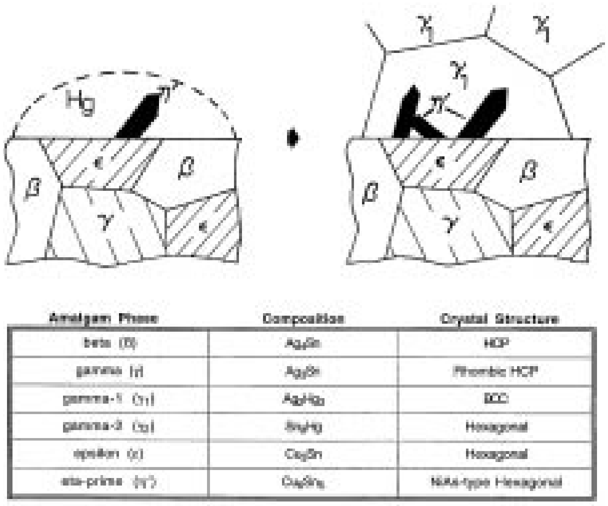
The resultant hardened amalgam is a metal-matrix composite in which alloy particles of approximately 30 vol % are embedded in gamma-1 (60%) and gamma-2 (10%) phases. The structure also contains unreacted epsilon (ε)-(Cu_3Sn) particles and voids in the gamma-1 matrix. Because of the low content of copper in this alloy formulation, gamma-2 phase is produced. This unwanted phase forms a galvanic couple with any silver not bound in the structure and readily corrodes in the mouth.

Okabe *et al.* [10] have studied the sequential mechanism of the amalgamation reaction in various alloys and have observed under scanning electron microscopy (SEM) that at high copper levels eta-prime (η')(Cu_6Sn_5) crystals precipitate out of solution before the gamma-1 (Ag_2Hg_3) base phase forms. The tiny, polyhedral, rod-like, η' crystals were found embedded within the grain boundaries of gamma-1 grains, giving support to the theory that they interlock with the grain boundaries to prevent plastic deformation, ostensibly by obstructing dislocation movement. This discovery is important since it demonstrates that the mechanical properties of amalgam are largely controled by the integrity of the gamma-1 base matrix.

The amalgamation reaction for admixed high-copper alloys proceeds as follows: when trituration begins, silver and tin dissolve into mercury from the gamma-(Ag_3Sn) and/or beta (Ag_4Sn) silver-tin phases. Silver also enters mercury from Ag-Cu eutectic particles and precipitates as gamma-1 (Ag_2Hg_3) grains. If sufficient copper is available, it will act as a sink for tin migration and combine preferentially with tin to form ultrafine eta-prime (Cu_6Sn_5) crystals rather than the unwanted gamma-2 (Sn_8Hg) phase. Formation of gamma-2 phase is totally suppressed by adding sufficient copper [8]. The reaction can be summarized as:

$$\begin{aligned} &Ag_3Sn\text{(gamma)} + Cu_3Sn\ \text{(epsilon)} + \text{Ag-Cu eutectic} \\ &\quad + Hg > Ag_2Hg_3 \quad \text{(gamma-1)} \\ &\quad + Cu_6Sn_5 \quad \text{(eta-prime)} \\ &\quad + \text{unconsumed particles} \end{aligned}$$

In the admixed alloy reactions, the eta-prime crystals nucleate at two different sites: (1) heterogeneously at the surface of the silver-copper eutectic particles and (2) homogeneously within the gamma-1 matrix. As the amalgamation reaction proceeds, a reaction layer 1–2 microns thick forms on the eutectic particle surface. This layer is a mixture of ultrafine eta-prime crystals and a lesser amount of gamma-1 grains. Saturation of silver occurs *after* formation of eta-prime crystals due to copper's low solubility in mercury. The base phase



Amalgam Phase	Composition	Crystal Structure
beta (β)	Ag_4Sn	HCP
gamma (γ)	Ag_3Sn	Rhombic HCP
gamma-1 (γ1)	Ag_2Hg_3	BCC
gamma-2 (γ2)	Sn_7Hg	Hexagonal
epsilon (ε)	Cu_3Sn	Hexagonal
eta-prime (η′)	Cu_6Sn_5	NiAs-type Hexagonal

Figure 1 Schematic view of the amalgamation of high-copper, single composition (Ag-Sn-Cu) powders. The powders form heterogeneous grain or phase structures shown. Eta-prime (η') crystals form (solid) first on the particle surface when wetted by mercury and then gamma-1 (γ_1) Ag_2Hg_3 grains form to create a matrix which includes the η' crystals. The phase compositions and crystal structures are noted.

gamma-1 (Ag_2Hg_3) precipitates out of solution as equiaxed grains, forming around and over the eta-prime crystals [8] (Fig. 1). The resultant structure of admixed high-copper alloys is a multi-phase metal matrix composite that includes unconsumed low copper alloy particles, unconsumed silver-copper eutectic particles and epsilon-(Cu_3Sn) particles, all embedded within the gamma-1 matrix. Thin eta-prime rod crystals, as previously described, are found within the gamma-1 grains [11].

In the amalgamation reaction of high-copper single composition alloy powders, Ag and Sn ions are released from the gamma and beta Ag-Sn equilibrium phases at the particle surfaces. Simultaneously, copper dissolves from the epsilon (Cu_3Sn) phase, which coexists with the silver-tin phases in the ternary Ag/Sn/Cu system. Tin atoms dissolved in the mercury are attracted to copper in the epsilon areas on the particle surfaces, forming meshes of eta-prime (Cu_6Sn_5) crystals on the unconsumed particles. The eta-prime crystals precipitate heterogeneously on the unconsumed particle surfaces as well as homogeneously within the gamma-1 grains. These crystals are known to impede plastic flow and improve creep resistance. It has been observed that the eta-prime crystals in these single-composition amalgams are much larger than those in admixed alloys [11]. The amalgamation reaction of single-composition high-copper alloys with mercury can be summarized as follows:

$$\text{Ag-Sn-Cu ternary alloy} + \text{Hg} > Ag_2Hg_3 \text{ (gamma-1)} + Cu_6Sn_5\text{(eta-prime)} + \text{unconsumed particles}$$

As in the admixed alloy, the resultant hardened structure contains unconsumed alloy particles, eta-prime crystals and the gamma-1 matrix [12]. Fig. 1 summarizes the amalgamation process schematically and shows the corresponding phase structures and compositions.

1.2. Alternative restorative systems

There have been a number of alternatives to dental amalgams. Common among these is gold foil which, although expensive, can be compacted directly into a cavity preparation. Gallium alloys were also developed in the past two decades, but their commercial success was short-lived because they lacked dimensional stability and corrosion resistance [13]. Because the mercury scare became especially prominent during the late 1980s and early 1990s, interest in other intermetallic alternatives to mercury-based systems grew. More recently, a cold-welded silver alloy system has been developed. This system, composed primarily of silver-coated Ag-Sn particles as 30–50 μm diameter spheres, can be condensed into a prepared tooth cavity in a manner similar to compaction of gold foil. A fluoroboric acid activating solution must be employed, however, to keep the silver surfaces clean; otherwise efficient bonding will not occur [14, 15]. Even with appropriately cleaned particles, compressive stresses required to form a cold-welded consolidated structure were more than an order of magnitude greater than that required to condense conventional mercury-containing amalgam, rendering the system unsuitable as a dental restorative material.

2. Experimental issues and procedures

In this study we explored several strategies for joining silver-coated particles as metal-matrix dental restoratives by producing interparticle amalgamation phases with mercury. The rationale for this approach was predicated upon the microstructural issues illustrated schematically in Fig. 2. By adjusting the particle sizes, and/or size distributions, as well as the powder mixtures, it may be possible to reduce the mercury content to be lower than in commercial dental amalgams (Fig. 1).

To accomplish this, the particle regimes must facilitate the efficient filling of space in a system where optimum sizes, distributions, and chemical mixtures are very complex. Fig. 2 illustrates the principal experimental systems. In Fig. 2(a) beta (β)(Ag_4Sn) and gamma (γ)(Ag_3Sn) phase particles coated with silver are mechanically joined in a fully dense restoration. As previously mentioned, this is not a viable approach since the required condensing forces are unreasonable. In Fig. 2(b) the Ag-coated particles in Fig. 2(a) are mixed with mercury and condensed, forming inter-particle gamma-1 (Ag_2Hg_3) phase. In Fig. 2(c) the Ag-coated Ag-Sn particles are mixed with Cu and Sn powders to fill interstices and promote eta-prime (Cu_6Sn_5) phase formation to strengthen the gamma-1 (Ag_2Hg_3) matrix phase. Fig. 2(d) shows the micrograph of experimental Ag-coated Ag-Sn particles in cross-section as observed in the SEM. These particles are the precursors for the consolidation illustrated schematically in Fig. 2(a), as well as the mixtures shown in Fig. 2(b) and (c).

Silver-coated particles illustrated typically in Fig. 2(d) were prepared by Materials Innovations, Inc., West Lebanon, NH, utilizing a patented process (U.S. Patent 5 603 815). In this process, previously atomized $Ag_{3.4}Sn$ particles are immersed in a silver cyanide electrolyte circulating over a vibrating cathode plate. Only particles with a diameter larger than 30 microns are used because

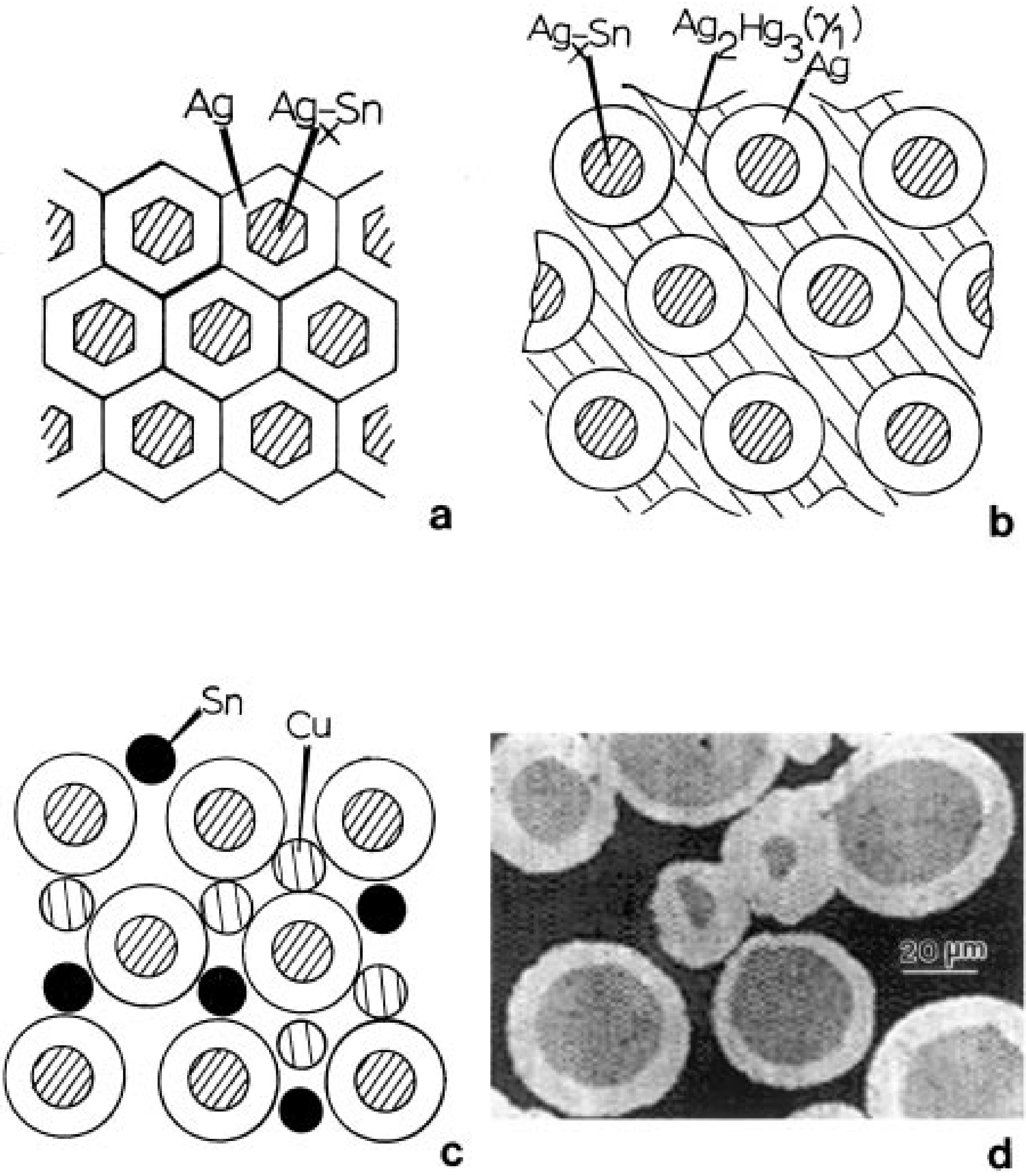


Figure 2 Particle/amalgamation strategies (a) ideal compression bonding/welding of Ag-coated, Ag-Sn core particles. (b) Amalgamation of Ag-coated, Ag-Sn core particles with Hg; forming Ag_2Hg_3 phase. (c) Powder mixture as in (b) containing Cu and Sn particles to promote Cu_6Sn_5 (η') crystal formation in the Ag_2Hg_3 inter-particle matrix. (d) Ag-coated, Ag-Sn core particles observed by optical microscopy (from [14]).

the smaller ones tend to stay in suspension. The vibration of the cathode in the fluidized bed cell causes a hopping, fluid-like motion of the particles, homogenizing the solution and facilitating the adsorption of silver onto the particles. The thickness of the silver coating, usually 5 microns or less, is controled by varying the electrical charge across the solution. Particles used in this study were prepared in batches with varying silver coating thicknesses with respect to the Ag-Sn particle core, and designated in weight per cent silver as 11, 16, 18 and 25%. Fig. 3 illustrates the typical as-received appearance of these particles.

For the preparation of amalgamated specimens, triple-distilled bulk mercury in varying amounts (ranging from 30–50 wt %) was mixed inside capped plastic capsules with each of the four Ag-coated particles (11%, 16%, 18% and 25%) and also with different combinations of Ag-coated particles with or without Cu and/or Sn powders. The Cu and Sn powders as shown in Fig. 4(a) and (b), respectively, were added to the alloy mixture in an effort to precipitate the important eta-prime phase (Cu_6Sn_5) out of solution during the amalgamation reaction. Amalgamation was accomplished with a Crescent Wig-L-Bug® mechanical triturator, using 10–20 s durations.

Commercial Tytin® control specimens (as shown in Table I) were amalgamated from pre-mixed 400 mg factory capsules. These Ag-Sn-Cu alloy particles are shown for comparison in Fig. 4(c). Some of the Ag-coated particles were warmed on a hot plate to about 50 °C in an effort to get better wetting with mercury. Significant amounts of mercury (30–50%) were used in

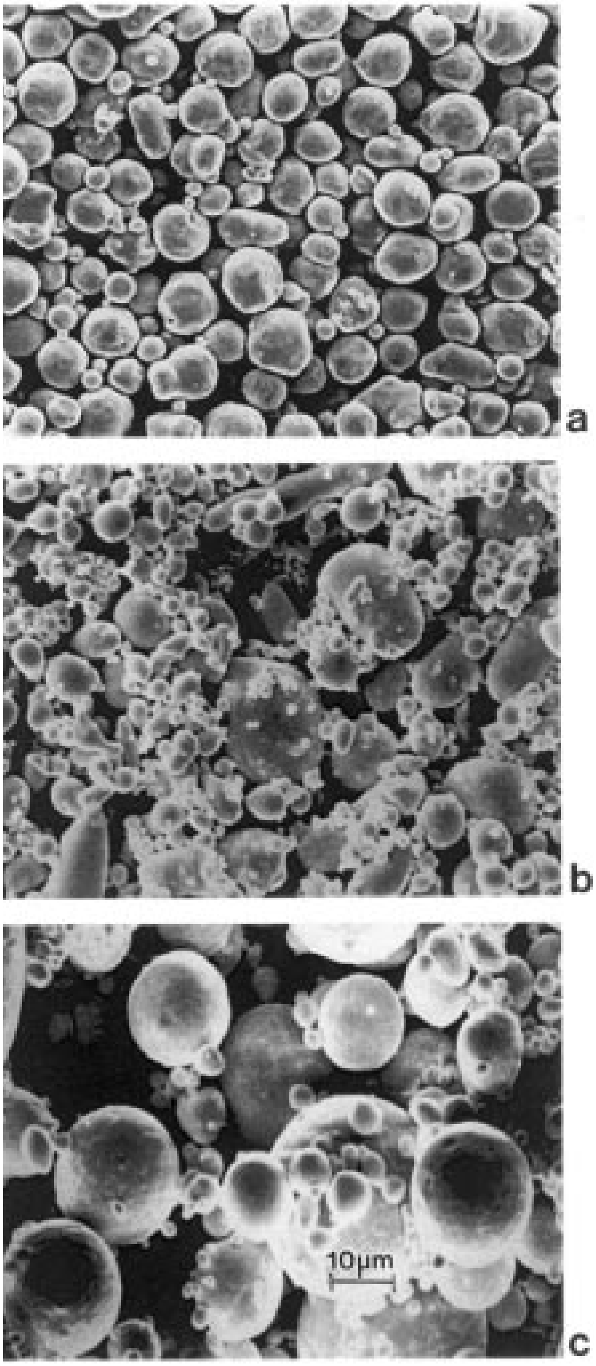


Figure 3 SEM views of powder particles. (a) Cu powder, (b) Sn powder, and (c) commercial Tytin® Ag-Sn-Cu powder (control).

order to examine conventional amalgam composition regimes and to assure maximum particle wetting for complete amalgamation. This range of mercury additions, especially between 40–50% is characteristic of that normally used with commercial amalgams, such as the Tytin® control and thereby provides a relatively equal mercury content for comparison and evaluation.

In an effort to remove the naturally-occurring surface oxides from the as-received particles and powders, three separate procedures were utilized: (1) the Ag-coated particles were heated to about 250 °C and furnace-cooled under a flowing argon gas atmosphere. After cooling to room temperature, they were crushed into powdered particles in a ceramic mortar and pestle (because they had fused in the furnace crucible) just prior to amalgamating with mercury; (2) the Ag-coated particles were acid-washed through standard filter paper with 10% acetic acid for about 5 min and air-dried for about 15 min prior to amalgamation with mercury; and (3) both Ag-coated and Cu-coated particles, as well as Cu and Sn powders, were acid-washed individually with 10% fluoroboric acid through a 10 micron pore ceramic funnel filter for about 5 min and air-dried for 15 min prior to mixing them in various combinations and amalgamating them with mercury.

Immediately after trituration, all amalgams were removed from the capsule and condensed into cylindrical 5 mm × 12 mm Plexiglas® molds with standard (2 mm diameter) dental condensing instruments and a manual force of about 10 pounds, and allowed to set and harden for 1 h. The hardened specimens, which generally weighed from 1.2 to 1.5 g, were removed and mounted in self-curing resin molds. After setting, their exposed surfaces were ground on a rotating drum with wet sandpaper from 240 to 1200 grit and then polished on cloth with 1 to 0.3 micron alumina slurries. The polished surfaces were etched with a 4 : 1 solution of ammonia water (NH_4OH) and 35% hydrogen peroxide (H_2O_2).

The prepared surfaces were characterized with light metallography, SEM and energy-dispersive X-ray spectroscopy for general microscopic features of the filler particles and surrounding matrix, surface chemistry across the interfaces and interphases, and integrity of the particle/matrix interface. Representative micrographs at different magnifications were taken to depict typical microstructural characteristics. The specimens then were tested for surface hardness with a Vickers diamond pyramid microhardness indentor with an included angle between opposite faces of the pyramid of 136° and a load of 50 gf (0.5 N). The machine automatically gave hardness readings from microscopic measurements of the lengths of the diagonals. Readings were recorded as Vickers hardness numbers (VHN) equivalent to units of kg/mm^2

For compression strength testing, both the control and coated specimens were amalgamated in the same manner as previously described, but condensed instead into the stainless steel die of a compression testing apparatus to form 4 mm × 10 mm cylindrical specimens. Specimens were expelled from the die mold about 2 min after the initiation of condensation. The testing apparatus was designed and constructed according to American Dental Association (ADA) specification No. 1 [16]. This apparatus basically involves a cylinder and plunger arrangement. The small cylindrical amalgam specimen to be tested is placed again in the test core and compressed with the plunger. Specimens were tested to failure in a standard Tinius-Olsen® tensile and compression testing machine (at a loading rate of about 0.5 mm per second) after a one-hour set in a 37 °C water bath.

3. Results and discussion

Utilizing the particle regimes illustrated in Figs 2d, 3 and 4a and b, as well as a regime of special particles made from 15 wt % silver on Ag-Sn cores coated with 20 wt % copper (Cu-coated particles averaging roughly 30 μm in diameter), specific regimes were mixed with mercury and amalgamated. Mixtures were also made with the Cu and Sn particles shown in Fig. 4a and b, in order to assure the formation of the eta-prime (Cu_6Sn_5) phase. However,

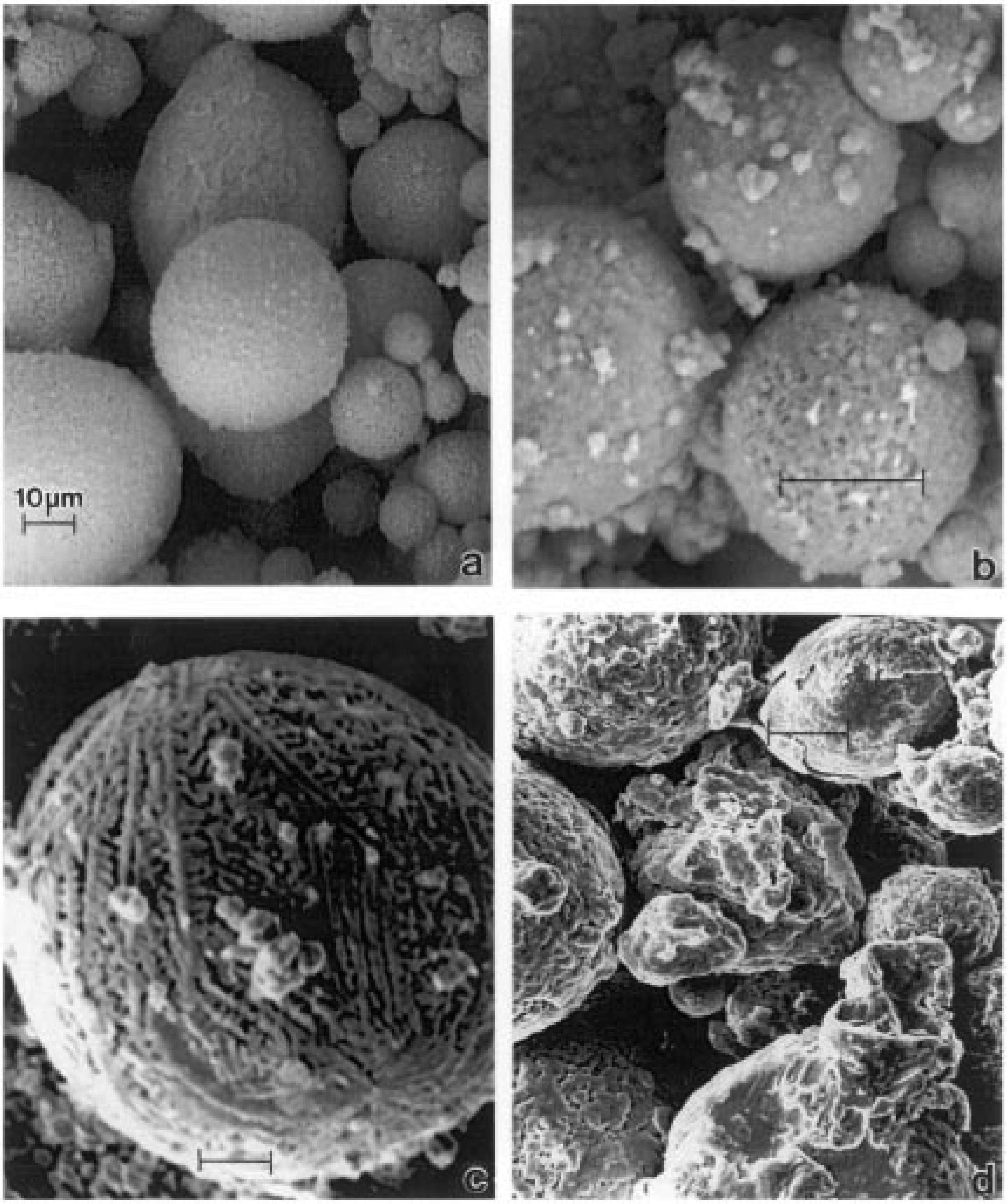


Figure 4 SEM views of experimental Ag-coated, Ag-Sn core particles: (a) 11% Ag, (b) 16% Ag, (c) 18% Ag, (d) 25% Ag.

only the Ag-coated or Cu-coated regimes achieved any amalgamation. The mixtures containing Cu and Sn particles did not achieve any degree of consolidated integrity primarily because of heavy oxidation especially on the Cu particles (Fig. 4a).

Three possible reaction phases can precipitate out of solution when conventional dental alloy particles (Fig. 4c) are amalgamated with mercury: gamma-1 (Ag_2Hg_3), gamma-2 (Sn_8Hg) and eta-prime (Cu_6Sn_5). In this alternative coated particle system, amalgamation with mercury of the 11%, 16%, 18% and 25% Ag-coated particles (Fig. 3), with or without the addition of Cu and Sn powders (Fig. 4a and b), produced the gamma-1 phase and possibly some gamma-2 as well, but no eta-prime phase.

Amalgamated microstructures for the four Ag-coated particle regimes are illustrated in Fig. 5. The interparticle matrix in the four micrographs is the gamma-1 (Ag_2Hg_3). As shown in Fig. 5c and d, relatively good particle/matrix cohesion was obtained with the 18% and 25% Ag-coated particles when mixed with 50 wt % mercury (1 : 1 ratio). This microstructural contiguity, however, did not necessarily produce strong specimens with high microhardness and especially compressive strength values, as shown in Fig. 6. Since the microhardness indentor was centered on the particle surfaces and did not include the gamma-1 (Ag_2Hg_3) interparticle matrix because of its mushy softness, particles with thinner coatings tended to register the higher readings, reflecting more closely the hardness of the Ag_4Sn intermetallic cores. These hardness values, therefore, could not be used to evaluate the consolidated integrity of the amalgamated specimens, but served instead to measure the contribution to hardness (or softness) by the thickness of the coatings.

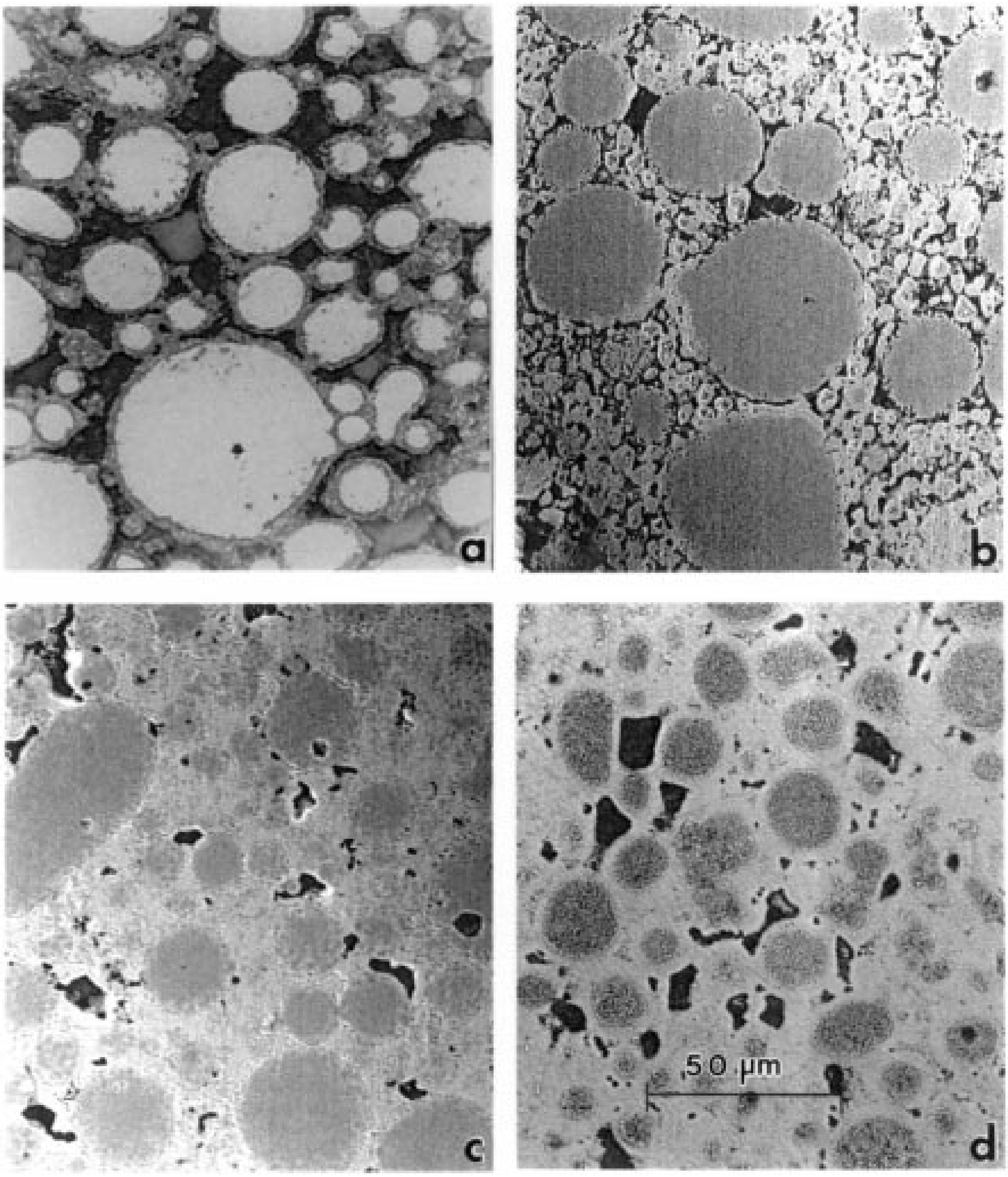


Figure 5 Optical microscopy and SEM views of polished experimental, consolidated Ag-coated, Ag-Sn core particles using 50% particles and 50% mercury mixtures: (a) 11% Ag, (b) 16% Ag, (c) 18% Ag and (d) 25% Ag. (a) is an optical micrograph.

Compression strength values (Fig. 6) on the other hand, are good indicators of the degree of cohesion at the particle/matrix interfaces. They also reflect the density and consolidated integrity of the interparticle gamma-1 base matrix. Since this system consistently lacked good chemical cohesion between the coated particles and their surrounding matrix, it was not surprising to note that specimens with the highest compression strength values were those that contained particles with silver satelliting (16 wt % Ag in Fig. 3b) and dendritic coatings (18 wt % Ag in Fig. 3c). These two particle regimes, unlike the 11 wt % Ag in Fig. 3a and 25 wt % Ag in Fig. 3d, which contained no physical means of retention, were able to produce mechanical interlocking at the particle/matrix interfaces as their principal mode of cohesion. This was accomplished by the formation of the gamma-1 phase around the silver satellites in the 16 wt % Ag-coated particle system and by the penetration of mercury between the dendrite branches in the 18 wt % Ag-coated system to form gamma-1 phase within and under the dendrites.

This novel mode of mechanical interlocking resulted in compression strength values of up to 40% of the Tytin® control. Except for one data point in Fig. 6, the experimental particle specimens were consistently stronger in compression when the alloy formulation contained the 18 wt % Ag-coated dendritic particles, ranging from 58 to 82 MPa. The second-highest compression strengths were recorded when the alloy formulation contained the 16 wt % Ag-coated particle specimens, ranging from 46–87 MPa. These compression strength values, although low when compared to the

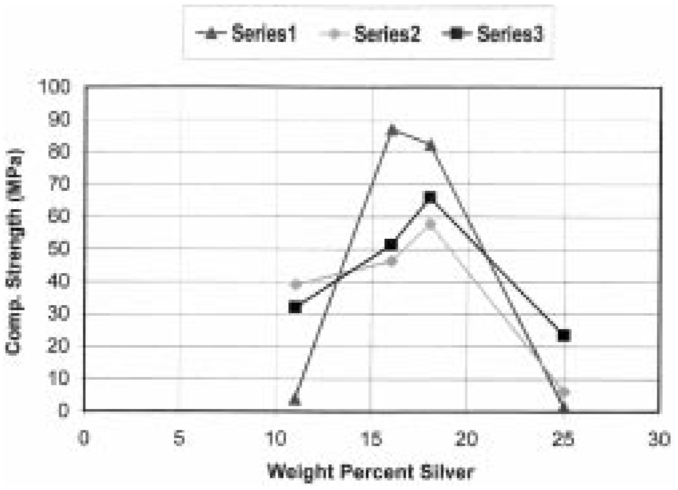


Figure 6 Average compression strength for experimental combinations utilizing wt % of Ag-coated, Ag-Sn core particles shown. (1): 60% Ag-coated particles + 40% Hg; (2): 30% Ag-coated particles + 30% Cu-coated/Ag-coated particles + 40% Hg; (3): 1/3 Ag-coated particles + 1/3 Cu-coated/Ag-coated particles + 1/3 Hg.

control, confirm that those particle systems that had silver satelliting and/or dendritic coatings formed the strongest specimens, ostensibly due to mechanical interlocking at the particle/matrix interfaces.

Comparing the single composition Tytin® control alloy to the experimental particle system, the control specimens consistently formed a dense monolithic microstructure with close cohesion of the unconsumed particles to the surrounding matrix, as shown in Fig. 7. This contiguity (Fig. 7a) is attributable in part to the interlocking of the gamma-1 base phase matrix around the eta-prime crystals, illustrated in Fig. 7b, that form on the particle surfaces and project into the interparticle space. The presence of these Cu_6Sn_5 eta-prime crystals at the control particle boundaries was verified by energy-dispersive X-ray spectroscopy as shown by the Sn and Cu density maps in Fig. 7e and f, respectively. Microhardness readings average 127 VHN in the control matrix compared to a very soft 43 VHN for the coated particle matrices, and 168 VHN for the unconsumed control particles versus a range of 60–142 VHN for the unconsumed experimental particles. One hour compression strength values averaged 210 MPa at a loading rate of 0.5 mm/second for the Tytin® control specimens, whereas the literature reports a range of 100 to 320 MPa for single composition alloys at a loading rate of 4.2×10^3 mm/second.

The proven commercial success of conventional dental amalgams can be attributed to the carefully engineered properties of the alloy powders by the manufacturers. Chief among these is the cleanliness and high surface energy of the particles that is imparted by acid washing and/or annealing in a reducing atmosphere. This is followed by encapsulation in a container filled with an inert gas, such as nitrogen, for preservation of the surface properties until the alloy is amalgamated in the dental operatory. This manufacturing strategy ensures that the alloy powders are not exposed to contamination from air until the alloy is ready to be used.

Overall, this study has demonstrated that development of a competitive amalgam alloy with conventional amounts of mercury additions will be difficult, and that to significantly reduce the necessary mercury content will be even more difficult. The results suggest, however, that a simple approach to improving existing amalgams by reducing mercury additions might involve the production of single-composition Ag-Sn-Cu particles with microdendritic structures similar to those shown in Fig. 3c. This would provide increased surface area in addition to the amalgamation interlocking features, possibly allowing for mercury reductions. The phase mixing to form the microcomposite structures shown schematically in Fig. 7b also appears to be a requisite feature for an optimized dental restorative material.

The reality of conventional dental amalgam is that in spite of mercury concerns, there is no compelling clinical data suggesting any major health problems arising from their use. Furthermore, composite resins and other esthetic restorative materials simply cannot match the wide range of microstructural and mechanical properties that serve to characterize dental amalgam as a superior dental restorative. Among these are high compressive strength, good creep resistance, high wear resistance, insolubility in oral fluids and the formation of corrosion products to help seal the margin at the tooth/amalgam interface. Berry *et al.* [17] recently concluded that dentists will continue to use amalgam as the restorative material of choice when esthetic concerns are not overriding.

4. Conclusions

The electrochemically-coated Ag_4Sn intermetallic particles used in this study appear to be viable alternatives to the conventional spray atomized and lathe-cut particles manufactured for dental amalgams. By controlling the oxide films and using particles with dendritic coatings, a dental alloy system with both mechanical and chemical retention can be developed. Such a system, by virtue of having both modes of particle/matrix cohesion, can substantially lower the mercury content needed to produce a strong amalgamated microstructure.

To accomplish this, a procedure must be devised in which the particles can be deoxidized and then immediately placed in containers that will protect them from reoxidation from air contamination. Also, the parameters in the electrocoating process must be adjusted to produce dendritically-coated particles that are smaller

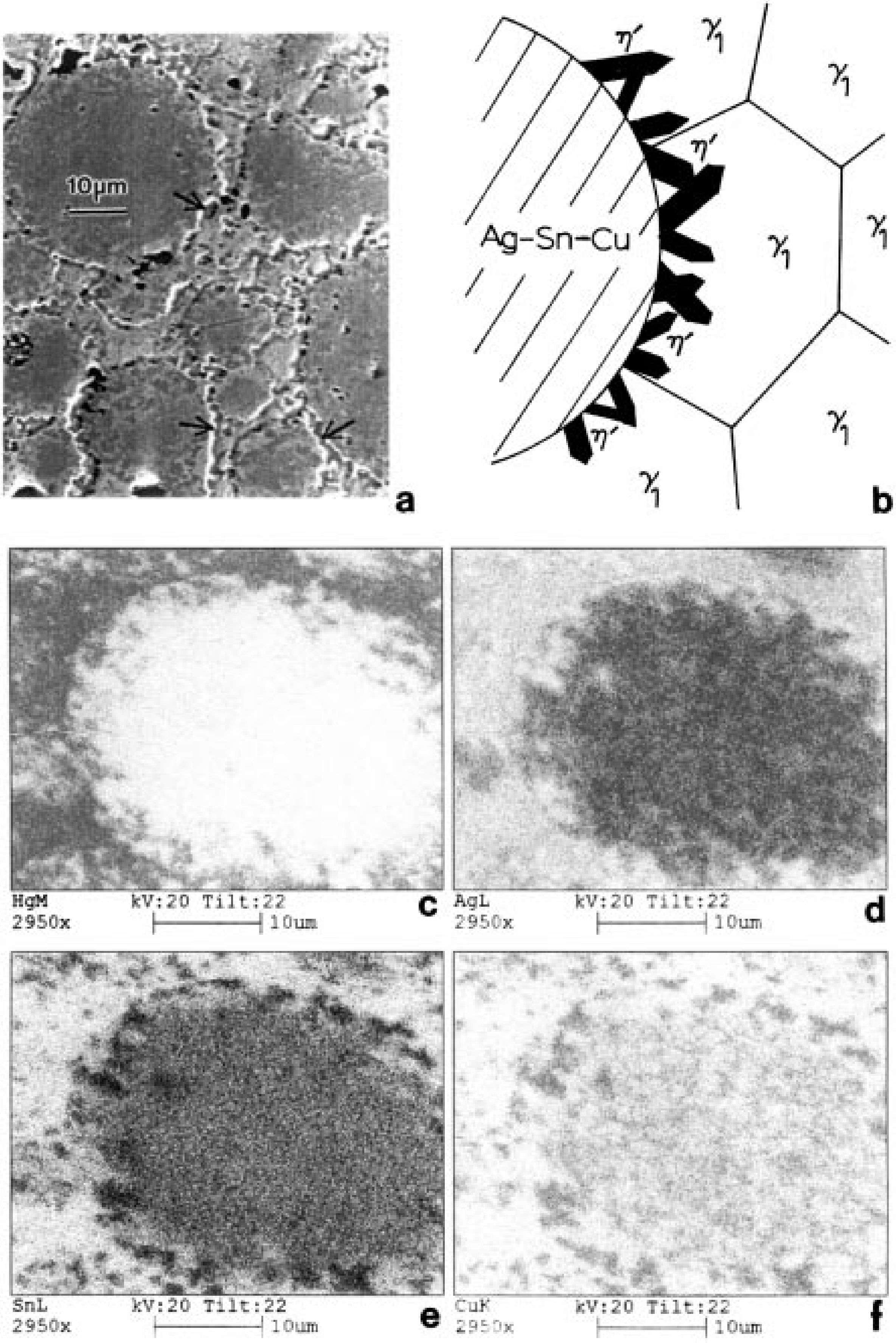


Figure 7 Amalgamation of the commercial (Tytin®) control showing the phase formation and inter-locking microstructures. (a) SEM view of consolidated amalgam. Arrows show η′-phase formation. (b) Schematic diagram showing the specific phase features observed in (c). (c), (d), (e) and (f) illustrate characteristic X-ray maps for large-particle region in (a) for elements Hg, Ag, Sn and Cu, respectively. Note Cu-Sn-rich phase region which surrounds the particle as shown schematically in (b).

and have a wider size distribution than the previous batches. This would enhance the packing efficiency, increase surface reactivity and eliminate voids and porosity in the amalgamated microstructure.

Despite anticipated improvements in this coated particle system, conventional silver amalgams will likely not be replaced in the near future. This venerable system, in spite of its mercury content, has served the dental profession well for over 160 years and produced restorations that have lasted 50 years or more. Other more aesthetically pleasing dental materials may continue to emerge in the market, but to date none have demonstrated the staying power of dental amalgams.

Acknowledgments

This research was supported in part by a Mr & Mrs MacIntosh Murchison Endowment at the University of Texas at EI Paso. We are grateful for the provision of experimental powders by Dr David Lashmore of Materials Innovations, Inc., West Lebanon, New Hampshire, and for his many interactions and discussions during the course of this research program. The help of David Brown of UTEP in the fabrication of the compression tester was also greatly appreciated.

References

1. E. GREENER, J. HARCOURT and E. LAUTENSCHLAGER, ''Materials in Dentistry'', (Williams & Wilkens Co., Baltimore, 1972).
2. W. O'BRIEN, ''Dental Materials: Properties and Selection'', (Quintessence Co., Chicago, 1989).
3. C. ROGGENKAMP, *Quintessence Int.* **17** (1986).
4. P. HORSTED-BINDSLEV, L. MAGOS, P. HOLMSTRUP and D. ARENHOLT-BINDSLEV, ''Dental Amalgam — A Health Hazard?'', 1st edn (Copenhagen, Munksgaard, 1991).
5. W. MCGEHEE, H. TRUE and E. INSKIPP, ''A Textbook of Operative Dentistry'', (McGraw-Hill Book Co. Inc., New York, 1958).
6. D. INNES and W. YOUDELIS, *J. Canadian Dent. Assoc.* **29** (1963) 587.
7. K. ASGAR, *J. Dent. Res.* **53** (1974) 23.
8. R. CAHN, M. BEVER (eds), in ''Encyclopedia of Materials Science and Engineering'', Supplement 2, (1990) 866.
9. T. BERRY, J. NICHOLSON and K. TROENDLE, *J. Amer. Dent. Assoc.* **125** (1994) 392.
10. T. OKABE, R. MITCHELL, M. BUTTS, A. WRIGHT and C. FAIRHURST, *J. Dent. Res.* **57** (1978) 759.
11. R. PHILLIPS, in ''Clinical Dentistry'', (1987) chap. 23, p. 9.
12. D. MAHLER, L. TERKLA, J. VANEPSDAN and M. REISBICK, *J. Dent. Res.* **49** (1970) 1452.
13. J. W. OSBORNE and J. B. SUMMITT, *Oper. Dent.* **76** (1997) 199.
14. M. DARIEL, D. LASHMORE and M. RATZKER, *Dent. Mater.* **11** (1995) 208.
15. F. C. EICHMILLER, A. A. GIUSEPPETTI and K. M. HOFFMAN, *J. Dent. Res.* **77A** (1998) 119.
16. ''Reports of Councils and Bureaus'', *J. Amer. Dent. Assoc.* **95** (1977) 616.
17. T. G. BERRY, J. B. SUMMITT, A. K. H. CHUNG and J. W. OSBORNE, *ibid.* **129** (1998) 1547.

Received 30 July 1999
and accepted 18 November 1999