

Rapid quenching of a commercial dental alloy

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A commercial silver–tin dental alloy (Ag_3Sn) has been rapidly quenched from the molten state in a controlled atmosphere “gun” splat quencher in order to obtain a chemically homogeneous structure and a fine grain size. The grain size obtained varies between 0.1 and 10 μm . Microstructural features have been examined by scanning and transmission electron microscopy. In very thin regions of as-quenched foils there is considerable faulting, but in slightly thicker regions, quenched-in dislocation loops are observed. The thickest areas of splats show dendritic structures and a cooling rate of 10^7 K s^{-1} can be estimated from the secondary dendrite arm spacings. Both X-ray and electron diffraction confirm that the crystal structure remains orthorhombic after very rapid quenching. Preliminary results on the effect of small grain size on amalgamation properties are reported and compared with powders that have been produced commercially.

1. Introduction

Since its inception rapid quenching from the melt has given rise to a wide range of new and interesting results which are traditionally classified under three headings:

(1) extension of terminal solid solution limits in excess of those predicted by equilibrium phase diagrams;

(2) new metastable crystalline phases;

(3) amorphous or microcrystalline materials.

The scope of alloys, techniques and results has been immense as evidenced by the bibliography of Jones and Suryanarayana [1], though the large majority of reported results are of academic interest only. One further spectacular result achieved by rapid quenching which is rarely reported, is the very small grain size produced in alloys which do not go to the extreme of microcrystallinity. Although the exact grain diameter is a function of alloy system and technique, the range of values varies between 0.1 and 5 μm for the “gun” technique of Duwez and Willens [2].

For the splat quenching process to be commercially viable with respect to a given alloy, the following criteria must be satisfied:

(1) The properties obtained must either be

unique to the rapid quenching technique, or alternative routes must be economically less favourable;

(2) although large scale quenching techniques are available [3], viable production quantities will be relatively small, and hence demand must be small and specific;

(3) rapidly quenched alloys must either be produced in a form that is useable without further manipulation, or consolidation processes need to be available which do not destroy any desired properties.

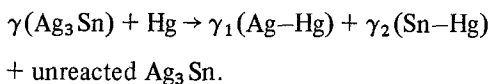
The purpose of the present research was to study an alloy system which would benefit from a small grain size, yet which complies with the above criteria. Silver–tin dental alloys are such a system. Traditionally these are prepared in two different ways. (1) The alloy is cast into rods which are subsequently cut on a lathe to produce a fine swarf. This swarf is mechanically comminuted to powder which is annealed prior to use. (2) Liquid alloy is atomized to give spherical particles which are then sieved to size. It is possible to insert splat quenching equipment in an existing atomization plant [3], and it can be

seen that all three routes are equivalent economically.

Both Ag–Sn and Ag–Sn–Cu alloys have been splat quenched by a rotating drum technique [26,27]. Whilst these studies were primarily concerned with application, superior properties in amalgams produced from the ribbon were shown for strength, corrosion and contraction criteria. The reason for these effects was attributed to the small grain size and large inherent defect population; however, Johnson *et al.* [27] reported difficulty in obtaining metallographic evidence to support these arguments. The present work attempts to survey metallographically the more simple Ag₃Sn dental alloy after rapid quenching in order to provide a basis for predicting amalgamation characteristics.

The silver–tin equilibrium diagram was investigated in detail by Murphy [5], who concluded that Ag₃Sn (γ phase) has a narrow compositional band (26.85 wt%) and is stable up to the peritectic temperature of 485°C. In general, dental alloys have a slightly higher silver content than this and contain some β phase (Ag₅Sn). Copper and zinc are often added to give ductility and corrosion resistance respectively. As chemical composition has a dramatic effect on “in service” properties, silver–tin dental alloys are covered by the American Dental Association specification No. 1. (Ag 65%, Sn 29%, Cu 6%, Zn 2% and Hg 3%) [6].

To make an amalgam, mercury is mechanically mixed with dental alloy powder (titration). The reaction between the two components has been described by Ryge *et al.* [7] as:



Hg reacts at high energy sites such as free surfaces and grain boundaries. Phillips [4] postulates that the two compounds formed have formulae Ag₂Hg₃ (γ_1) and Sn₇₋₈Hg (γ_2) respectively. The amounts of each of these phases is dependent upon the amount of mercury added and the particle and grain size.

2. Experimental techniques

It is generally recognized that the “gun” technique of Duwez [2] affords the highest cooling rates when quenching from the liquid state. In the present study, a controlled atmosphere gun,

capable of quenching alloys with melting points up to 1700°C [8], was employed. 200 mg samples of commercial dental alloy (kindly donated by the Amalgamated Dental Company), were inserted in an alumina crucible with a 0.4 mm diameter orifice in its base. The gun was enclosed in a sealed chamber and was evacuated to 10⁻⁴ Torr before pure argon was admitted to a partial pressure of 500 Torr. Samples were heated to 1000°C before ejection onto a roughened, water cooled, copper substrate. The landing area was approximately 10 cm from the orifice. Thin foils and powder were removed for subsequent investigation.

The alloy had a chemical analysis as follows: 69.8 Ag, 25.4 Sn, 4.1 Cu and <0.1% Zn. Samples of “lathe cut” and splat quenched powder were examined by X-ray diffraction using an 11.48 cm diameter Debye–Scherrer camera with Straumanis mounting. Samples were exposed to cobalt $K\alpha$ radiation from a 2 kW tube for 5 h. Metallographic examination of foils was performed on a Cambridge Instruments Ltd. “Stereoscan Mk II” and on a JEOL “JEM 200” transmission electron microscope operating at 200 kV. The hardness of foils and amalgamated samples were measured on a Leitz “Miniload” tester.

Foils were powdered in a ball mill and passed through a 50 μm sieve before amalgamation. Amalgams were made by mixing known quantities of powder and mercury in a centrifugal mixer and then consolidated into $\frac{1}{8}$ in. diameter holes in a brass block by an experienced dentist.

3. Results

3.1. Scanning electron microscopy

As the molten alloy is ejected through the crucible orifice it atomizes into small droplets whose diameter is dependent upon the surface tension of the alloy. The resultant splat quenched foil is produced by the consolidation of these droplets on the substrate as can be seen in Fig. 1. The droplet sizes fall in the range 10 to 30 μm in diameter, which is consistent with those measured for pure silver by Predecki *et al.* [9], and for atomized dental alloys [10]. At higher magnifications the grain structure can be resolved (Fig. 2), and a mean grain size of 5 μm is observed although the range of diameters varies between 0.25 and 10 μm . This is an order of magnitude smaller than grain sizes found in conventional powders.

No macrosegregation is detectable in splat

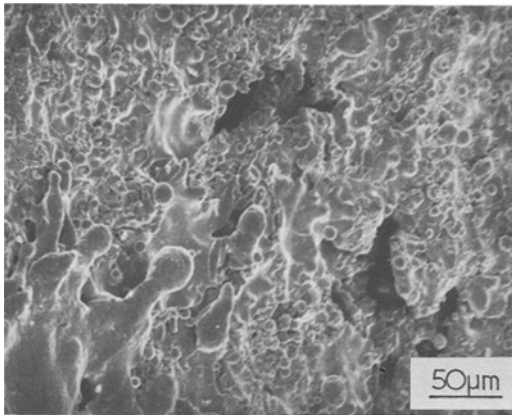


Figure 1 Low magnification scanning electron micrograph showing the consolidation of atomized droplets of Ag_3Sn to form a coherent splat foil.

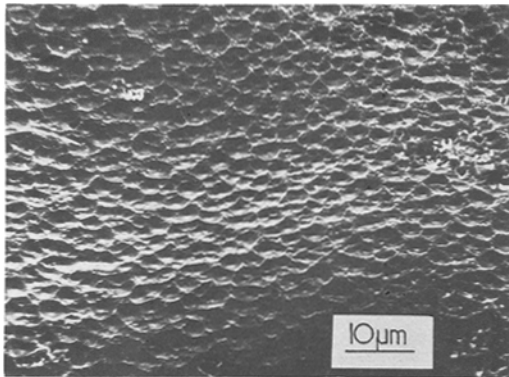


Figure 2 Scanning electron micrograph – unetched. Grains within a splat of dental alloy.

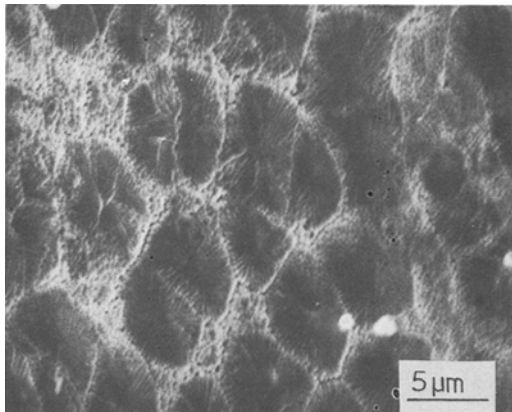


Figure 3 Scanning electron micrograph – unetched. Dendritic growth within grain corresponding to a local cooling rate of approximately 10^7 K sec^{-1} .

quenched foils, but in larger grains dendritic growth is detectable (Fig. 3) with tin rich interdendritic regions. The mean secondary dendrite arm spacing is $0.35 \mu\text{m}$, which was obtained by

the technique of Levy *et al.* [11]. Whilst no data are available for the dependence of secondary dendrite arm spacing on cooling rate for Ag–Sn alloys, the results of Matyja *et al.* [12] for aluminium alloys give a value of $\sim 10^7 \text{ K sec}^{-1}$ for the above measurement. Further, this result is consistent with cooling rates determined for other alloy systems on the present apparatus [8].

3.2. Hardness

Foils that were thick enough for testing give a mean hardness value of 380 V.P.N., compared with a value of 230 V.P.N. for as-received material. This is an increase of 65% for the splat quenched samples and can be attributed to the Hall–Petch grain size effect and to the greater chemical homogeneity of splat quenched foils.

3.3. X-ray diffraction

Powder patterns from both splat quenched and lathe cut powder were identical with respect to the lines present and their relative intensities. Whilst the lines were somewhat diffuse, it was possible to ascribe an orthorhombic structure to the splat quenched powder with lattice constants:

$$a = 2.99(9), b = 5.18(8) \text{ and } c = 4.84(8) \text{ \AA}$$

3.4. Transmission electron microscopy

In all foils produced by splat quenching, regions were thin enough for TEM study without further preparation and Fig. 4 is typical of the microstructure which is seen in thinnest regions. Such areas are identified by long thin elongated grains lying normal to the electron beam and have been characterized in terms of local heat flow conditions by Wood and Sare [13]. Grain A shows a form of faulting in regions of maximum contrast. Fig. 5 is a detail from one such grain showing this effect more clearly. Separate bands of these faulted regions can be highlighted in dark-field and it is probable that they are microtwins. Electron diffraction patterns from these areas confirm the orthorhombic structure derived from X-ray measurements. At the top of grain B (Fig. 4) small dislocation loops are visible. These are found in slightly thicker regions of transparent areas and are more extensively shown in Fig. 6a. The corresponding diffraction pattern is shown in Fig. 6b indicating a $[1\bar{4}1]_{\gamma}$ zone. Precipitate spots are evident along $[0\bar{1}4]$, $[10\bar{1}]$ and $[212]_{\gamma}$

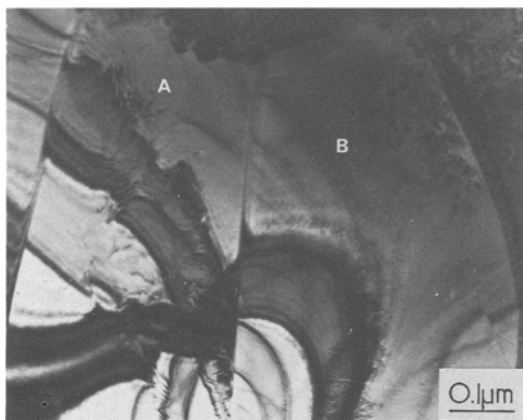


Figure 4 Transmission electron micrograph. General view with elongated grains lying perpendicular to the electron beam.

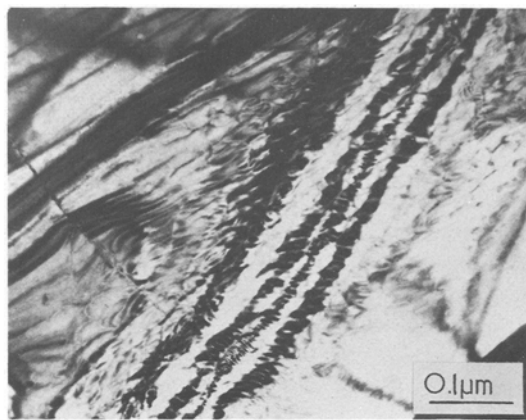


Figure 5 Transmission electron micrograph. Detail of heavily faulted grain found in very thin regions of sputter quenched Ag_3Sn foils.

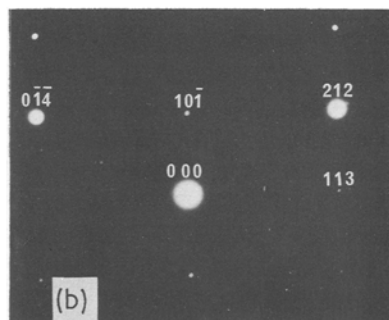
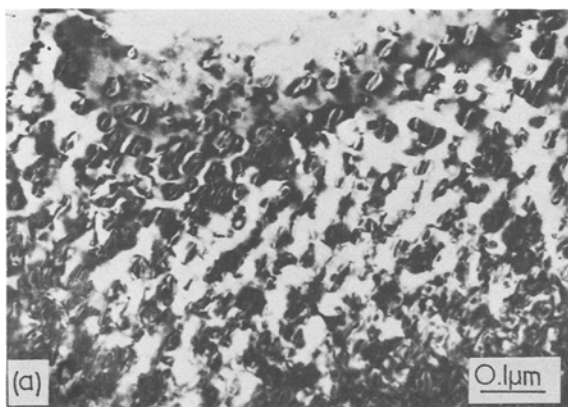


Figure 6 (a) Transmission electron micrograph of dislocation loops in unthinned regions of Ag_3Sn foils. (b) Electron diffraction pattern from (a).

directions. In dark-field these illuminate globular surface oxide which is inherent in the as-received ingot. Surface oxide could sometimes be observed in SEM studies, confirming this proposition. No evidence was forthcoming to suggest that these “looped” areas contained extremely fine precipitate.

3.5. Amalgamation

Detailed measurements were not possible due to the small amounts of powder available, but some preliminary observations are reported. The main variables are mercury: alloy ratio, tituration time, and compaction pressure. The last two were kept constant and four Hg: Ag_3Sn ratios were employed between 1.06 Hg: 1.0 Ag_3Sn and 1.75 Hg: 1.0 Ag_3Sn (by weight). The total weight of the resulting amalgam was 400 mg (the ratio for conventional lathe cut powders is 1.1). The low ratio produced a crumbly amalgam and the high mer-

cury amalgam started to approach the consistency necessary for moulding into cavities. After ageing for 1 week from compaction, amalgam made from conventionally produced Ag_3Sn powder had a hardness of 240 V.P.N., whilst the high Hg-splat amalgam had a hardness of only 100 V.P.N. The scatter of results was very large and the difference in these values is attributable to the difficulty in compacting splat amalgams. Fig. 7a and b show unetched optical micrographs of splat amalgams at low and high Hg levels respectively. The structure consists of large unreacted γ (Ag_3Sn) particles surrounded by γ_1 and γ_2 phases. As the Hg level is increased, γ_2 grows into large particles whilst the morphology and distribution of γ_1 remains unchanged (Fig. 7b). Fig. 7c is a micrograph from a standard commercial amalgam. The more uniform microstructure is a result of the greater ease of compaction compared with splat amalgams.

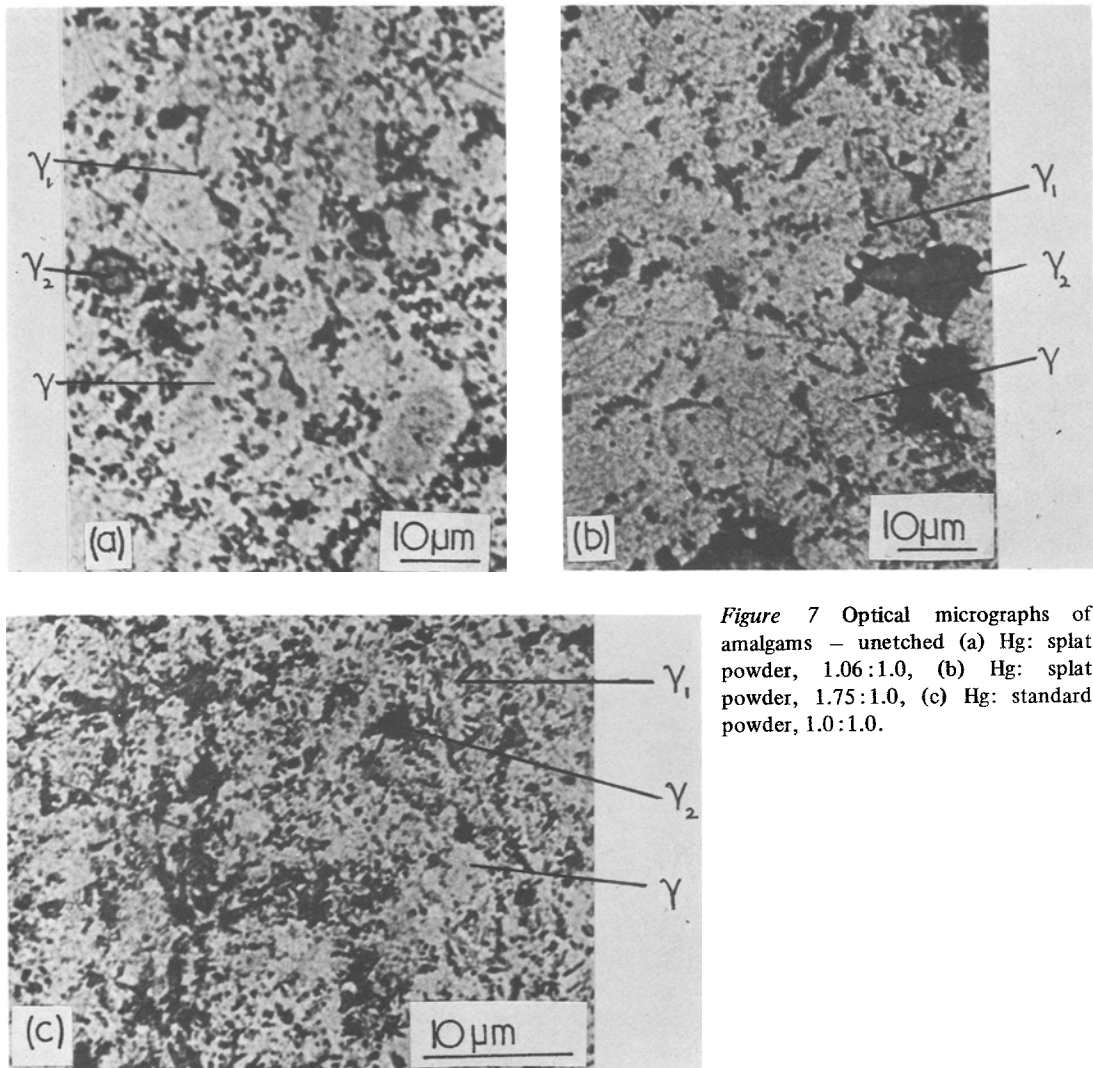


Figure 7 Optical micrographs of amalgams – unetched (a) Hg: sput powder, 1.06:1.0, (b) Hg: sput powder, 1.75:1.0, (c) Hg: standard powder, 1.0:1.0.

4. Discussion

Present results confirm those of Johnson *et al.* [27] that γ phase is the only phase present after rapidly quenching Ag_3Sn . It appears therefore, that Ag_3Sn must nucleate directly from the melt due to sufficient undercooling to avoid initial β nucleation ($\sim 180\text{ K}$).

Dislocation loops have been observed in sput quenched fcc metals [14,15] and alloys [16]. These have been formed by the nucleation of vacancy clusters from the matrix, which had been supersaturated with respect to vacancies by rapid quenching from the melt. Bolling and Fainstein [17] have shown that it is energetically possible for vacancies to nucleate in a number of systems when rapidly quenched, and to grow into dislocation loops of vacancy type. Whilst it was not

possible to unambiguously determine the nature of the loops in Fig. 6a they can be assumed to be vacancy in nature in line with previous work. Further, it has been shown by Thomas and Willens [14] that in splatted aluminium foils less than 1500 \AA thick, no vacancy loops are observed because vacancies can diffuse to free surfaces before being quenched-in. Fig. 4 shows a similar situation although the critical thickness has not been determined in the present case. In these very thin regions it is, therefore, necessary to accommodate the thermal strain induced by quenching by an alternative mechanism to dislocation movement which is evident in thicker areas, if the elastic limit of the material has been exceeded. In the present case this is achieved by faulting (Fig. 5) and this result is consistent with observations for other

alloy systems [18, 19].

Dislocations dissociate readily in Ag_3Sn deformed at room temperature [20] but no stacking faults were observed in rapidly quenched Ag_3Sn . In isomorphous Al_3Ni plastically deformed at temperatures greater than $0.85 T_m$ (melting point) dislocations do not dissociate [21]. Extending this observation to the present system, it can be postulated that plastic strain in quenched foils occurs significantly at high temperatures without dislocations dissociating into partials.

It was not possible to determine the exact nature of the faulting in very thin areas by electron diffraction, although it was possible to isolate parallel bands within faulted grains by reciprocal lattice spots lying along some $\langle 011 \rangle_\gamma$ directions. Fairhurst and Cohen [22] observed deformation markings on the surfaces of Ag_3Sn single crystals. These were shown by X-ray diffraction to be twins on $(0\bar{1}1)$ and (011) planes, with shear directions $[0\bar{1}\bar{1}]$ and $[0\bar{1}1]$ respectively, although it was necessary to postulate an atomic shuffle to preserve the ordered structure. As the present results are consistent with these specific results, it is probable that the faulting in Fig. 5 is a form of microtwinning.

The exact crystal structure of Ag_3Sn has long been in dispute, having been variously described as "multiple hexagonal" [23], and "deformed hexagonal" [24]. The present lattice parameters derived by X-ray diffraction are compared with those of two other proposed orthorhombic structures for Ag_3Sn in Table I. The present work does

TABLE I Comparison of orthorhombic lattice parameters for Ag_3Sn

Reference	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$
Nial <i>et al.</i> [22]	2.98	5.149	4.771
Fairhurst and Cohen [24]	5.9688	4.7802	5.1843
Present work	2.99(9)	5.18(8)	4.84(8)

not substantiate the larger value determined by Fairhurst and Cohen. Compositional differences and specimen preparation are sufficient to account for the small discrepancy between our values and those of Nial *et al.*

As larger amounts of Hg are needed to form acceptable amalgams with splat powder, this suggests that mercury reacts faster than with commercial powders. Since the particle size distribution between splat and commercial powders is the same, this increase in reactivity is directly

attributable to the increase in grain-boundary area. It is not favourable clinically to add large amounts of free mercury as this increases the final amount of unreacted mercury in the amalgam at constant condensation pressures. Both γ_1 and γ_2 reduce the strength of amalgam, and thus the large γ_2 particles (Fig. 7b) found at high mercury levels are also undesirable. It has been shown [25] that very fine Ag_3Sn particles give rapid hardening amalgams which have better dimensional stability than amalgams formed with larger particles, but they do suffer from very large initial shrinkages. This shrinkage can be overcome by further balancing of the chemical composition of the initial alloy [4].

5. Conclusions

The following results were obtained for a splat quenched commercial dental alloy.

(1) Rapid quenching from the liquid state does not alter the equilibrium solid state crystal structure which can suitably be described as orthorhombic.

(2) The range of grain sizes varies between 0.1 and $10 \mu\text{m}$, with a mean of $5 \mu\text{m}$.

(3) In electron transparent regions no segregation is detected, but dendritic growth can be observed in larger grains. This latter structure is assumed to have cooled at a slower rate of about 10^7 K sec^{-1} .

(4) In electron transparent regions of unthinned foils, the thinnest crystals exhibit faulting which is probably microtwinning. In slightly thicker regions excess vacancies are retained in solution during solidification and subsequently collapse to form vacancy loops.

(5) The hardness of splats is 65% higher than normal commercial alloy powder.

(6) Splat powder reacts faster with mercury than commercial powder and this is directly attributable to the reduction in grain size.

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