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Production of dental alloy by the melt extraction technique

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Filaments of a commercial dental alloy (Ag_3Sn) have been produced using the technique of pendant drop melt extraction. The filaments are 50 μm in diameter with a mean grain size of 5 μm. Both the mechanical and structural properties of these wires have been determined to show that the results are consistent with those predicted in a previous study on small flakes made by the "gun" splat quenching technique. The ultimate tensile strength and ductility of these wires are significantly superior to samples made by chill block casting. Simple amalgamation experiments have been undertaken to confirm that alloys made in this way would be acceptable in practical situations.

1. Introduction

For many years silver–tin dental alloy powders have been titurated with mercury to form amalgams which harden with time after insertion into pre-drilled dental cavities. A number of alternative materials have been put forward in order to minimize the amout of mercury employed, but this system is still the most widely used in practice. Whilst the composition of the alloy powder is essentially Ag_3Sn, both zinc and copper are added for corrosion resistance and dimensional stability after amalgamation. Mercury is mixed with fine dental alloy powder (either produced mechanically or by atomization) to form two related intermetallic phases from Ag_3Sn (γ), namely Ag_2Hg_3 (γ_1) and Sn_7Hg (γ_2) [1]. Mercury is thought to diffuse along grain boundaries rapidly to produce the amalgam slurry, and then to slowly react with the Ag_3Sn grains. The reaction does not proceed to completion, thus leaving particles of γ surrounded by γ_1 and γ_2.

In recent years a number of techniques have become available to produce long lengths of rapidly solidified ribbon or wire [2]. By the technique of rapid solidification a very small grain size and a high vacancy supersaturation can be obtained [3]. Data on melt-spun Ag–Sn–Cu alloys have been obtained by Johnson *et al.* [4] with reference to the corrosion and contraction properties of the resultant amalgams. The present work seeks to expand the fundamental structural work of Wood and Jacombs [3] on a commercial dental alloy to large scale production of rapidly cast wires by the melt extraction technique [2].

2. Experimental

2.1. Preparation

Dental alloy was kindly supplied by the Amalgamated Dental Company with the following composition: 69.8 Ag, 25.4 Sn, 4.1 Cu and $<0.1\%$ Zn. This alloy was chill-cast into 10 mm diameter rods under argon. These rods were inserted into a pendant drop melt extraction apparatus [2]. A droplet was melted on the end of the rod by a radio frequency induction heater. The drop just touched the periphery of a fast rotating copper disc with a sharp edge profile. A fine diameter wire was drawn from the drop and collected in a water filled container 30 cm from the droplet. Details of the present arrangement and the effect of certain variables have been described elsewhere [6]. Approximately 1 kg of material was cast in this way in 5 min. Although in the present arrangement fine wire was cast, it is possible by notching the periphery of the rotating wheel to produce a fine powder [5], and this could be used to cast dental alloy powder directly. However, it was assumed that the resulting material would show the same

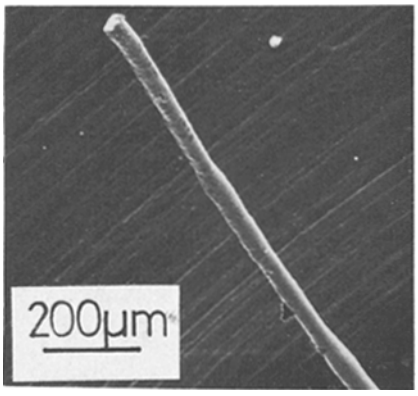

Figure 1 Scanning electron micrograph showing a typical Ag_3Sn wire cast by the melt extraction technique.

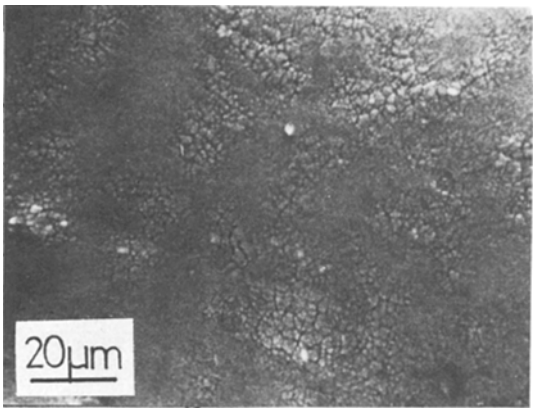

Figure 2 Surface of filament (unetched) showing apparent grain size or dendrite clustering (scanning electron micrograph).

characteristics in both cases. The (Ag_3Sn) wire (produced by this technique) is of the order 50 μm in diameter (±5 μm) and a typical example is shown in Fig. 1.

2.2. Mechanical testing

Both tensile and hardness tests were performed on the "as-cast" wire. The former were conducted on a Techne Instruments Whisker tester designed by Marsh [7]. This enabled data to be gained from short samples (typical gauge length 1 mm) which had a reasonably consistent cross-sectional area. The samples were glued onto silica grips with "Araldite" and allowed to harden for two days. In all cases the load was applied to a value below the yield point and then it was removed to ensure no slipping of the specimen in the grips. Yielding could be detected above certain critical loads when the specimen continued to deform with time for a given increase in load. In these cases the specimen was left for 30 sec before the extension reading was taken and then the load was increased. The hardness of both wires and resultant amalgams were measured on a Leitz "Miniload" tester.

2.3. Structural assessment

Grain size measurement and fracture surfaces were observed on a Cambridge Instruments Ltd. "Steroscan II". Crystal structure of the "as-cast" wires was checked in a Debye–Scherrer powder camera using CuKα X-radiation.

2.4. Amalgamation

The "as-cast" fibres were chopped by rotating steel blades to form a powder. The powder was passed through a 58 μm sieve before quantities were weighed for amalgamation. Mixing of the powder and mercury was performed in a mechanical pestle in current use by dentists. After mixing for various times the amalgam was hand pressed into pre-drilled holes in a stainless steel block.

3. Results

3.1. "As-cast" fibres

X-ray diffraction shows that γ is the only phase present in the extracted fibres with orthorhombic lattice constants: $a = 2.97$, $b = 5.17$, and $c = 4.77$ Å. Some very thick wires (~ 120 μm in diameter) were accidentally made where the droplet slipped from the edge of the wheel. However these too exhibited no phase other than γ thus indicating that it is relatively easy to suppress β from coming out of solution.

The grain size can be determined by direct observation of the surface of the wire in a scanning electron microscope. Fig. 2 shows such an area. Whilst each of the lobes appear to be about 2 μm across, careful observation shows that they are often clustered together (typically in groups of four) and it is thus assumed that the lobes are dendrites within grains and that the actual grain size is about 5 μm in diameter.

The hardness of the wires was approximately 350 V.P.N. It was felt that tensile tests yielded more useful data and thus hardness was only assessed to compare the wire with those of previously rapidly solidified flakes (380 V.P.N. [3]). The data for a total of four tensile tests are summarized in terms of their mean values in Table I. The wire was assumed to be of circular cross-section

TABLE I Mean values for tensile tests on melt extracted Ag_3Sn

Diameter (μm)	Young's modulus (MN m^{-2})	0.001% proof stress (MN m^{-2})	U.T.S. (MN m^{-2})	Elongation (%)
48	2.3×10^4	210	340	1.75

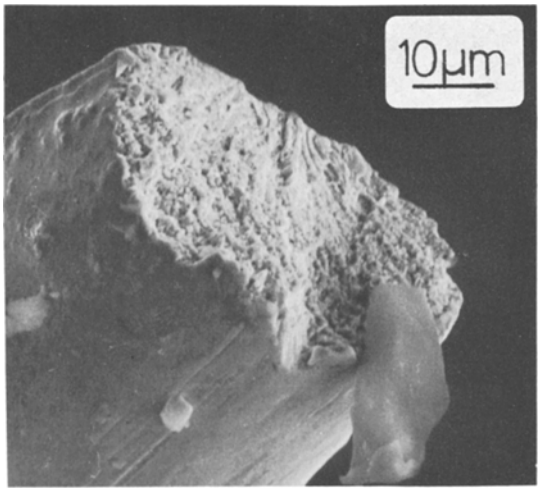

Figure 3 Fracture surface of tensile specimen.

in calculating modulus and stress values. In reality the wires are slightly kidney-shaped with a longitudinal flute running along the wire where the edge of the mould drags the fibre from the pendant drop. Thus values quoted could be between 5 to 10% too low, depending on the exact geometry of the wire.

A proof stress is quoted in preference to a yield point as stepwise loading of the sample can easily hide the true onset of yielding, which in any case is extremely small in this normally brittle material. The fracture surface of one sample is shown in Fig. 3. There appears to be some slight necking consistent with the measured ductility, and the surface is fibrous in nature. The grain size and shape might well account for this appearance, though there is some evidence from an anomolous fracture surface (where the grain size was excessively large) to suggest that failure is intragranular (though in the case cited the failure was distinctly crystallographic in nature). However, the dimpling is of the same order of the dendrite arm size (see Fig. 2) suggesting that localized flow can occur along chemically inhomogeneous regions within each grain.

3.2. Amalgamation

Three mixing times (15, 30 and 60 sec) and three mercury: powder ratios (0.75, 1.00 and 1.25) were used to ascertain the kinetics of the amalgamation reaction and the resultant microstructures. The physical nature of the amalgam is important in application with a stiff slurry being the ideal consistency. Amalgams with low mercury concentrations (0.75) tended to become crumbly after short times and thus become impossible to consolidate, whilst the high Hg levels after short times are too slushy to be manageable in practice. The microstructures from all nine amalgams are shown in Fig. 4, showing clearly the dark reacted phase in the matrix of light γ as a function of mixing time and mercury concentration.

The hardness of amalgams was measured after ageing at room temperature for two weeks. Essentially the hardness is determined by two conflicting interests: (i) enough reaction to effectively "glue" the γ particles together, and (ii) minimization of the volume of low strength γ_1 and γ_2 phase. Hence hardness values of amalgams are plotted against Hg: Ag_3Sn ratios for different times in Fig. 5. Thus it can be seen that the best ratio is 1 : 1 where the reaction proceeds fairly fast yet gives consistently high hardness values.

4. Discussion

Whilst it has been suggested recently that the cooling rate directly influences grain size [8], it would appear from the present work that the grain size in melt extracted Ag_3Sn is not markedly different to that found in Ag_3Sn produced by "gun" splat quenching although there are at least two orders of magnitude difference in cooling rate [9]. It is therefore postulated that, since the substrate material is the same for both apparatuses (copper roughened with 400 grade emery paper), the undercooling of the alloy in each case is the same thus allowing the same density of nuclei to form. As the wire is rapidly ejected from the wheel in solid form, it is to be supposed that the initial cooling rate for both through the liquid to solid reaction is the same though there could be a considerable difference in solid state cooling rates. Assuming that there is no time for subsequent grain growth, the only difference between alloys

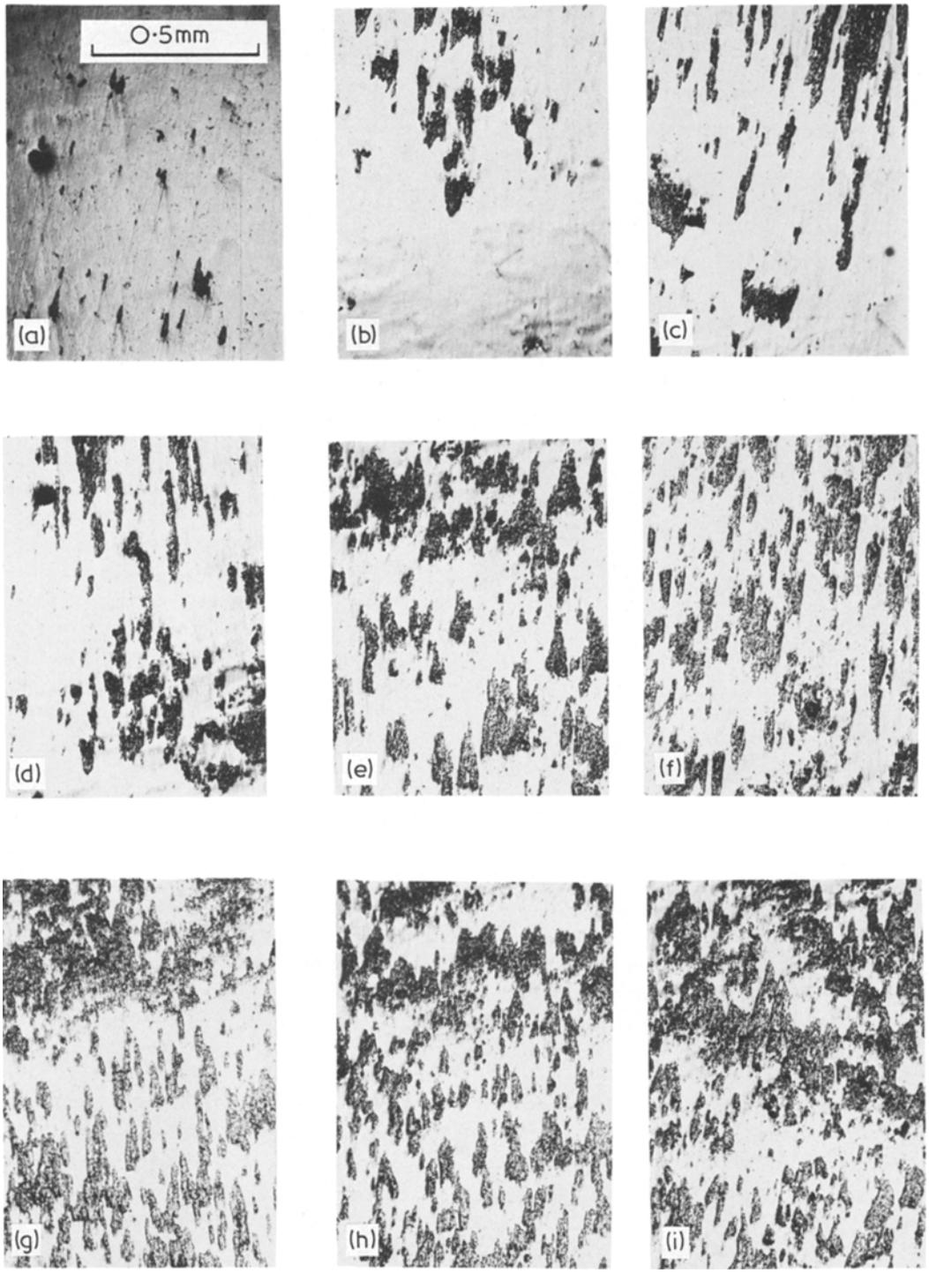

Figure 4 Unetched amalgam samples showing light γ phase and dark γ_1 and γ_2 phases for different Hg:Ag_3Sn ratios and different mixing times. (a), (b) and (c) have a Hg:Ag_3Sn ratio of 0.75, and mixing times of 15, 30 and 60 sec respectively; (d), (e) and (f) have a Hg:Ag_3Sn ratio of 1.0, and mixing times of 15, 30 and 60 sec respectively; (g), (h) and (i) have a Hg:Ag_3Sn ratio of 1.25 and mixing times of 15, 30 and 60 sec respectively. All photographs are at the same magnification.

produced by the two techniques will be in the excess quenched-in vacancy concentration as no second phase is detected in either.

Young and Wilsdorf [10] have measured the tensile strength of Ag_3Sn after slow cooling and chill casting. Fortunately they published micrographs of the resulting structures which has enabled an estimation of grain size to be made. These results and those of the present work are portrayed in Fig. 6 which is a plot of U.T.S. against grain size. Using the typical equation that:

$$\sigma_F = \sigma_i + k_F d^{-\frac{1}{2}}$$

(where d is the grain size) the results of Young and Wilsdorf enable values for the constants to be estimated, namely:

$$\sigma_i = 145\,\text{MN m}^{-2} \text{ and } k_F = 0.215\,\text{MN m}^{-3/2}$$

Whilst there is some error in the grain size measurements of Young and Wilsdorf they are insignificant when compared with the effect of a small change of grain diameter within the rapidly quenched alloy. Thus using the above constants the melt extracted wire should have a mean grain size of 1.7 μm. However it has already been stated that the grain size is more probably ~5 μm corresponding to a U.T.S. of 240 MN m^{-2}. The observed increase of U.T.S. could be ascribed to either the effect of the large increase in vacancy concentration [3] or that the U.T.S. is more dependent on secondary dendrite arm spacing at these very small grain dimensions. For metals with a vacancy formation energy ~1 eV, the resultant vacancy concentration after rapidly quenching from the melt is about 10^{-3} [11]. It has been shown [3] that this large excess vacancy population formed in "gun" splat-quenched Ag_3Sn collapses to form sessile vacancy loops about 100 Å in diameter analogous to a dense precipitate. Dislocations normally dissociate in Ag_3Sn [12] at room temperature under tension, thus adding to the problem of unpinning in the present situation.

Young and Wilsdorf state that in all tensile tests the elongation of Ag_3Sn was less than 1%. In the present case the value of 1.75% is thus relatively high by comparison. If dislocation movement is so difficult in conventional alloys it is unlikely that with more obstacles it will be easier in rapidly quenched alloys. Superplastic behaviour has been reported in rapidly solidified alloys with a fine grain size [13]. Whilst 1.75% elongation can hardly be described as superplastic, the strain rate using the whisker tester is relatively low thus allowing some grain boundary or interdendritic sliding. Technologically this increase in ductility is probably more important than the increase in strength.

It can be seen that the best ratio of Hg to Ag_3Sn is 1 : 1 by volume, which is the current practice for conventionally produced powders. Johnson *et al.* [4] have measured the tensile of strength of melt spun Ag_3Sn, when amalgamated at the above ratio and mixed for 20 sec, as 52 MN m^{-2}. Young and Wilsdorf [10] have given tensile strength values for γ_1 and γ_2 as 14 and

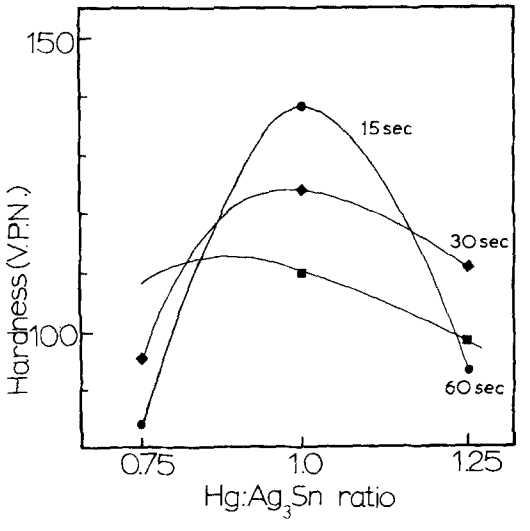

Figure 5 Hardness against Hg:Ag_3Sn ratio for different mixing times.

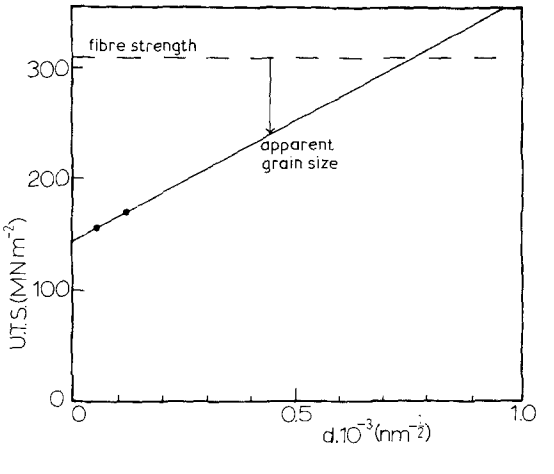

Figure 6 The effect of grain size on the ultimate tensile strength of Ag_3Sn cast by different techniques.

21 MN m^{-2} respectively. Using a simple law of mixtures this would lead to only 23% γ remaining. This is clearly not true as can be observed in Fig. 4e (the nearest equivalent microstructure). It would be more reasonable to suggest that γ_1 and γ_2 cover 77% of the total grain boundary area (assuming now that failure is intergranular).

5. Conclusions

(1) Rapid quenching of a commercial dental alloy by the pendant drop melt extraction technique gives a fine grained structure (grain size $\sim 5\mu m$) which exhibits a large increase in strength over chill cast alloy (94%).

(2) This increase in strength is accountable to a combination of grain size and dislocation pinning effects.

(3) A significant increase in ductility has been measured which also depends on the very fine grain size produced.

(4) The best amalgam is produced with a mercury to alloy ratio of 1:1.

(5) Using the pendant drop melt extraction technique to cast dental powders directly would appear to offer superior alloy powder properties over those produced by alternative techniques and also be more economical in operation.

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