Backscattered electron imaging of dental amalgam

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A study of the microstructure of set dental amalgams has been undertaken using techniques of back-scattered electron imaging, transmission electron microscopy and X-ray analysis. It has been demonstrated that small ($\approx 0.2 \mu$m) particles of a copper–tin phase are present in the matrix of the conventional low-copper amalgams and that the reaction zone around the silver copper eutectic phase in the high copper dispersion type amalgams is of a duplex nature consisting of the Cu_6Sn_5, η' phase and an intervening layer of silver–mercury phase.

1. Introduction

Although the first recorded use of dental amalgam as a filling material in dentistry dates back as far as 1826, and the subsequent extensive clinical use has been paralleled by very active research into the structure–property relationships in this complex material, the precise nature of the microstructure of amalgam is still a matter of controversy. The interest in this subject, which might have been perceived to be declining some ten or so years ago, has been revived in recent years with the development of different formulations which give variations in structure and significant improvements in properties, especially the corrosion resistance. These differences are largely associated with variation in the amount of copper that is included in the alloy which is mixed with mercury to form dental amalgam.

Since the comprehensive work of Black [1] at the beginning of this century, the dental profession has used an alloy of approximate composition 65 to 70 wt % silver, 25 to 27 wt % tin, 0 to 6 wt % copper and 0 to 2% tin. This composition essentially corresponds to the γ phase (Ag_3Sn) of the silver tin system, an orthorhombic structure, although possibly with traces of the β phase. This alloy reacts with mercury in a reaction which is generally described by the following equation [2–4]

$$Ag_3Sn + Hg \rightarrow Ag_2Hg_3 + Sn_{7-8}Hg \qquad (1)$$

$$\gamma \qquad\qquad\qquad \gamma_1 \qquad\quad \gamma_2$$
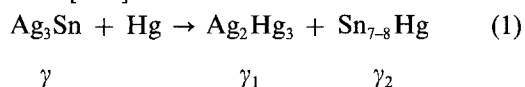
The mixture usually contains an excess of the γ phase so that approximately 30% of this phase is present in the set material, an important consideration in terms of the development of strength during the reaction. The reaction product phases are Ag_2Hg_3, the γ_1 phase of b c c structure, and $Sn_{7-8}Hg$, a random solid solution of mercury in a hexagonal tin lattice.

Some of the most important features of the amalgam metallurgy are the role of copper in the reaction, the adverse effects of the γ_2 phase on the resulting properties, and the relationship between these two aspects. As noted above, a small amount of copper may be present in the initial alloy used, and it has not been clear how this copper is distributed in the set amalgam. It is now well known that the γ_2 phase, being predominantly of tin, contributes unfavourably to the corrosion and creep properties of amalgam [5–7]. In experiments aimed at improving mechanical properties of amalgam by introducing a dispersion hardening effect associated with Ag–Cu eutectic particles intentionally added to the alloy [8] it was found that copper, when present in sufficient quantity, is able to significantly reduce or eliminate entirely the γ_2 phase and substitute in its place Cu_6Sn_5 (η'), an orthorhombic superlattice of the NiAs type. Thus an important relationship between the copper content of amalgams and their properties has been established. In spite of some extensive and excellent work, however, it is still not entirely certain how this copper relates to the various phases in set amalgams. This paper presents some more experimental data on this question.

The very complex nature of the amalgam microstructure demands that high spatial resolution techniques are used in its study. However, there are significant problems of specimen preparation with these mercury-based materials in the context of electron optical techniques. Very few attempts have been made, for example, to study amalgam by transmission electron microscopy. In this paper we report some observations made by conventional TEM but concentrate on the technique of backscattered electron imaging (BEI). This is of particular relevance since the backscattering coefficient of any material is dependent on the atomic number so that, with a spot size of 10 to 20 nm, high resolution imaging, with a contrast that is dependent on the chemical nature of the material, is possible.

2. Materials and methods

Two commercially available amalgams were used in this study. The first was an example of a conventional, low-copper amalgam Amalcap^R, (Vivadent, Lichtenstein, Batch 030480 1546), supplied in predispensed capsules with a mercury to alloy ratio of 1 : 1.1. The

second was Dispersalloy[R] (Johnson & Johnson, Slough, Batch 030380 B 013815), a high-copper variety also supplied in predispensed capsules with a mercury to alloy ratio of 1 : 1. In both cases amalgams were prepared using a Silamat high speed amalgamator at 5 sec. Cylinders of 3 mm diameter were prepared using a Perspex split mould and hand condensation. Cylinders were removed from the mould and allowed to stand for 3 h in a dessicator. 500 μm thick sections were then prepared from the central area of the cylinder using a lubricated, diamond impregnated blade, and these were ground and polished on both sides to a 0.25 μm finish using standard techniques.

For TEM, cleaned specimens were placed in an Ion Tech ion-beam thinner. The amalgams were not readily thinned in this way and at the optimum conditions of a low (10 to 15°) incident angle and low (3 to 4 kV) voltage, thinning times of at least 14 days resulted. For this reason specimens were ground to 50 to 100 μm thickness before ion-beam thinning and some areas suitable for TEM were obtained with Amalcap. Most specimens were too brittle to manipulate after ion beam thinning.

For the BEI technique, similar 200 μm thick specimens polished to 0.25 μm finish were initially used. The complex microstructure that included some relatively soft areas resulted in a widespread distribution of scratches even after extensive polishing. Totally scratch free specimens were impossible to prepare but, using a 0.03 μm particle size alumina, some scratch-free areas in samples were obtained.

Specimens were examined using a Phillips 400T analytical electron microscope fitted with an EDAX detector and backscattered and secondary electron detectors. BEI was carried out with a 20 nm probe size at 40 kV. Normally backscattered electron detectors yield an output where bright areas are of high atomic number, while the dark areas are of low atomic number. In these experiments the detector was reversed so that areas of elements with high atomic number were seen to be dark and those with low atomic number were seen to be light.

3. Results

The general appearance of the microstructure, as seen in backscattered electron imaging, of the conventional dental amalgam is reproduced in Fig. 1a. This, along with higher power micrographs of the phases present reveals some features not previously described. In Fig. 1b a residual γ particle is shown, where dissolution can be seen to be directional, following the dendritic structure of this phase. In Fig. 1c, γ phase is seen within the particles. The γ_1 matrix contains numerous 0.1 μm, irregularly shaped areas (Fig. 1d).
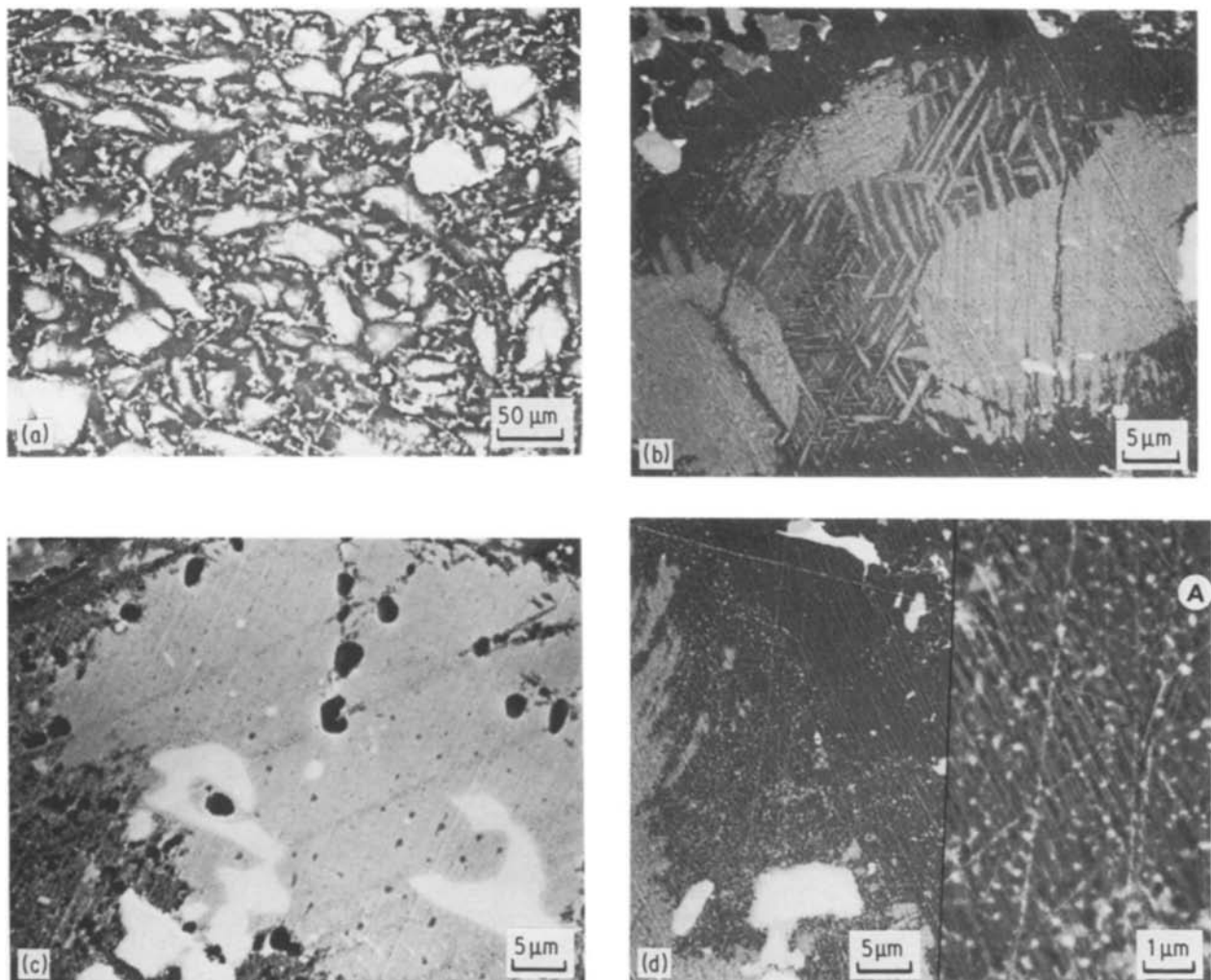

Figure 1 BSE images of conventional dental amalgam. (a) General structure, (b) residual γ particle in γ_1 matrix, (c) interface of γ and ε phase with the γ matrix, (d) dual magnification image of the γ matrix.
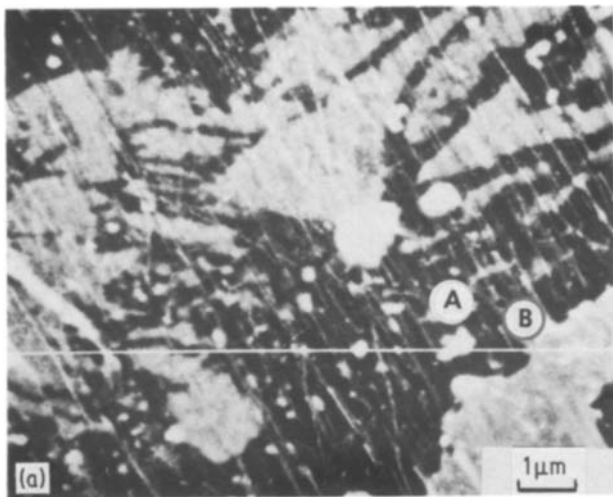
(b)

These areas were subjected to semi-quantitative X-ray analysis. Fig. 2a shows a representative area in the region of a residual γ particle and in Fig. 2b the line scan, giving relative elemental concentrations, may be seen. The residual γ phase (Ag_3Sn) is seen to the left, with γ_1 matrix (Ag_2Hg_3) in the centre and γ_2 phase (Ag_7Hg) to the right. The small particle at A in the γ_1 matrix appears to be relatively rich in copper and tin.

Higher power examination of other areas confirmed this observation. Some of these areas were also observed within the γ_2 phase.

Bright field TEM revealed a grain size of around 0.3 μm in the γ_1 phase (Fig. 3a). These grains were heavily faulted (Fig. 3b). Small electron opaque particles were frequently seen in the γ_1 matrix, which EDAX confirmed as being copper-rich (Fig. 3c).

Low magnification back scattered electron imaging of Dispersalloy revealed the type of general microstructure reported previously (Fig. 4a). Higher resolution micrographs demonstrated the eutectic nature of the silver–copper phase (Fig. 4b). The reaction zone between these eutectic particles and the matrix was also demonstrated to be complex (Fig. 4c), with four regions (A–D) being evident. A and D represent eutectic and matrix, respectively, and B and C are the regions within the duplex reaction zone. An EDAX line scan (Fig. 4e) on the particle shown in Fig. 4d
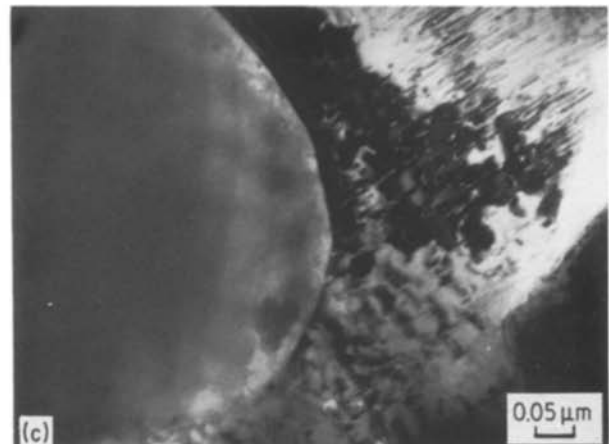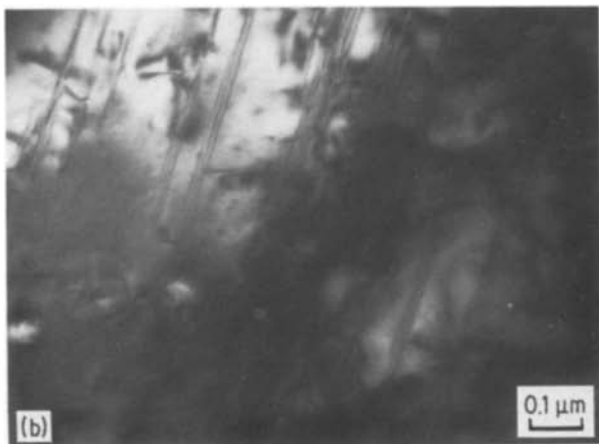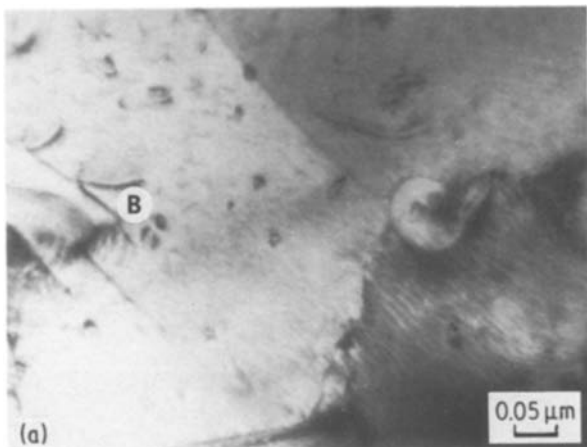

Figure 3 Bright field images of conventional dental amalgam. (a) The γ_1 phase, (b) heavily faulted grain structure, (c) copper rich particle in γ_1 matrix.
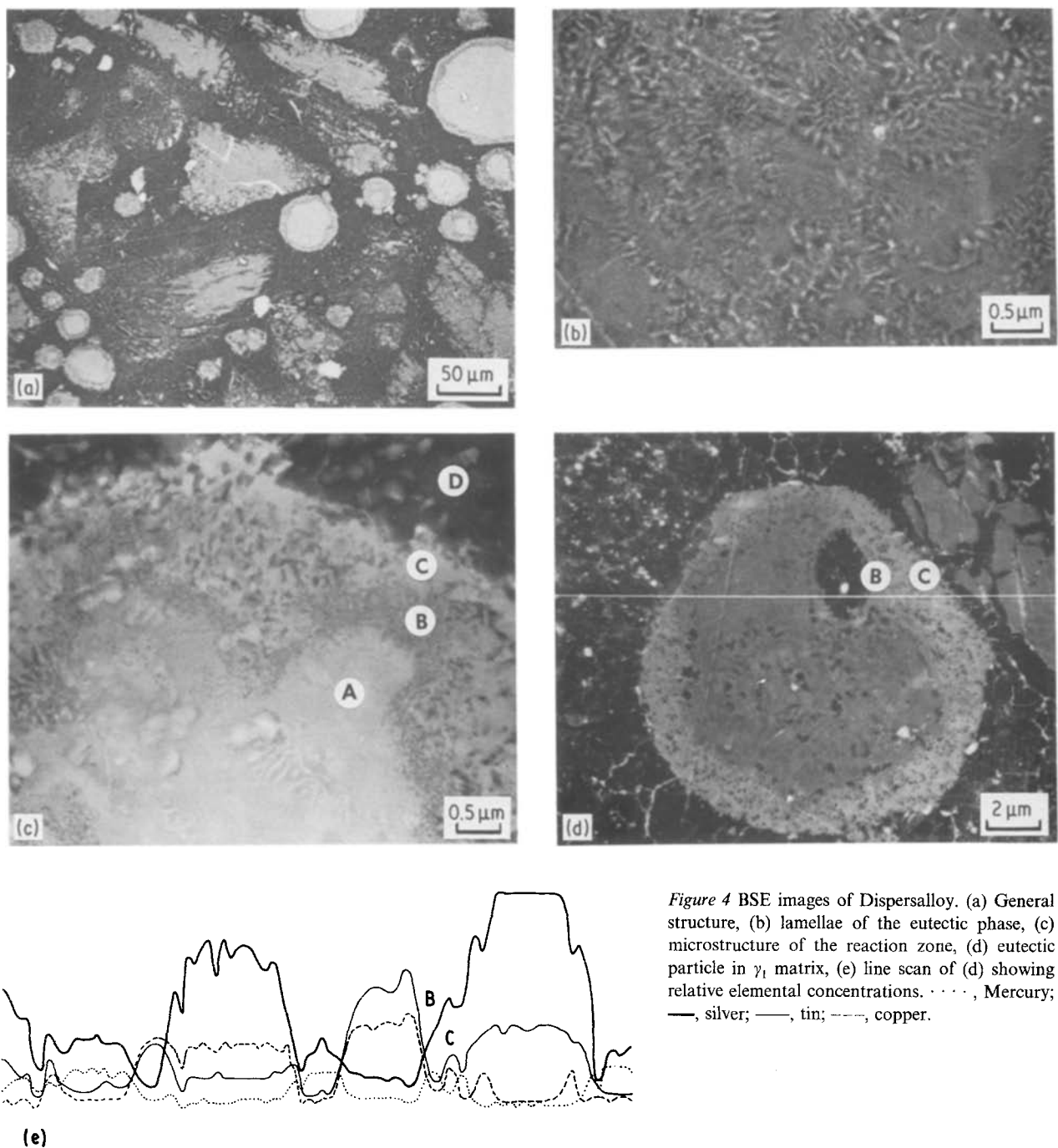
Figure 4 BSE images of Dispersalloy. (a) General structure, (b) lamellae of the eutectic phase, (c) microstructure of the reaction zone, (d) eutectic particle in γ_1 matrix, (e) line scan of (d) showing relative elemental concentrations. · · · ·, Mercury; ——, silver; ——, tin; ———, copper.

clearly shows the silver–copper eutectic particle, the γ (silver–tin) particle to the right and the dark silver–mercury γ_1 matrix. The reaction zone appears to have two components, being predominantly of copper–tin, but with a thin zone of the silver–mercury between the eutectic and the copper–tin η'.

4. Discussion

This study has revealed that within the microstructure of set conventional amalgam, which contains only a small amount of copper, are small copper–tin phases, occurring both in the γ_1 matrix and also in the γ_2 particles. Sutfin and Ogilvie [9] have previously indicated that copper was present in the γ_2 phase but they were unable to resolve any copper-rich phase in the matrix. Crowell [10] has also pointed out that a small amount of copper could form as a new discrete phase in the matrix which he assumed would be Cu_3Sn (ε). Work of Johnson *et al.* [11], Jensen and Anderson [12]

and Vrijhoef and Drissens [13] has also suggested that formation of some copper–tin phases during the setting of amalgam and Okabe *et al.* have recently demonstrated the production of the η' (Cu_6Sn_5) phase on high temperature ageing [14]. These present observations confirm these conclusions and demonstrate quite clearly the existence of discrete phases approximately 0.1 μm diameter, of a copper–tin phase.

The back scattered imaging of the higher copper Dispersalloy has also demonstrated the structure of the reaction zone between the silver–copper eutectic particles and the γ' matrix. Okabe *et al.* [15] have previously discussed the reaction zone and suggested that it was of a duplex nature. The present study has demonstrated at least two different structures within the reaction zone. The inner region is similar to the lamellae of the eutectic whilst the outer region has a much coarser grain size. Much of the reaction zone consists of a copper–tin phase as expected, but an

inner region of a silver–mercury phase, presumed to be γ_1, has been identified. It is likely that this duplex structure arises because tin diffuses very slowly from the γ phase [16] while silver is able to diffuse much more quickly out of the silver–copper eutectic.

5. Conclusions

The present work has, through the use of back scattered electron imaging and X-ray analysis, demonstrated the presence of copper–tin phases in the γ_1 matrix of conventional low copper amalgam. The duplex nature of the reaction zone of the higher copper dispersion type amalgam has also been clarified.

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