Letters

The suppression of γ_2 precipitation and the kinetics of the gettering of Sn in a dispersed-phase dental amalgam

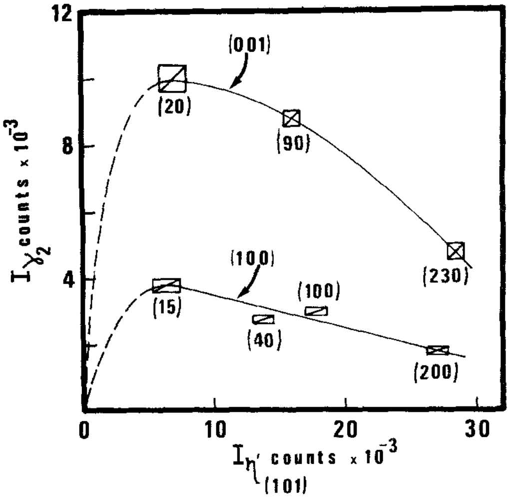

Figure 1 Integrated intensities, $I_{(hkl)}$ of selected X-ray powder reflections (hkl) for the γ_2 and η' phases in Dispersalloy amalgams during ageing at 300 K. Monochromatic Cu$K\alpha$ radiation; $\frac{1}{4}°$ min^{-1}; 40 kV; 35 mA; specimen area 120 mm^2. Numbers in parantheses specify the time in minutes elapsed from trituration. The ratio $I^{\gamma_2}_{(001)}/I^{\gamma_2}_{(100)}$ varied between specimens due to differences in the degree of preferred orientation of γ_2 crystals arising in surface layers having slightly different Hg concentrations. Small variations in the condensation procedures were probably responsible for the variable Hg segregation. The figure gives measurements for specimens showing the largest and smallest γ_2 intensity ratios. These ratios remained unchanged during ageing indicating that the time variation in I corresponded to changes in the volume fraction of γ_2. Intensities were estimated using a computer-based peak-stripping, background subtraction procedure.

The amalgamation of Ag–Sn-based dental amalgam alloys involves the liberation of Sn which, in the presence of appreciable amounts of Cu, can precipitate as the η' (Cu_6Sn_5) phase instead of as the mechanically weak and easily corroded γ_2 ($Sn_{7-8}Hg$) phase [1–11]. In the case of commercially available dispersed-phase powder blends, the Cu is mostly present in Ag–Cu–Sn "additive" particles which are usually spherical in shape. The other component of the blends are spherical, lathe-cut or micro-cut Ag–Sn "alloy" particles having little or no Cu. For additive particles with compositions close to the Ag–Cu eutectic composition, the η' in the set amalgam is primarily located within the Asgar–Mahler [1, 2] reaction zones. These zones result from the transformation of the surface layers of the additive particles to a microduplex mixture of small ($< 0.5\,\mu$m diameter [5, 6]) grains of the η' (70 to 85 wt% [4, 6]) and γ_1 (AgHg) phases. Only a small proportion of the η' arises as sub-micron sized precipitates located throughout the γ_1 matrix [8–11].

Fig. 1 shows some measurements of the integrated intensities of selected η' and γ_2 X-ray powder reflections during the ageing of a dispersed-phase amalgam (Dispersalloy: Johnson and Johnson, New Jersey) at 300 K. It can be seen that the γ_2 intensity passes through a maximum at about 20 min. This result indicates that the γ_2 forms in the presence of a residual Hg solution for it has been established that liquid Hg persists in the amalgam mix for about 30 min after the initiation of trituration [10, 12–14].

The liquid-phase sintering of the dispersed-phase amalgam can be divided into two stages. The first involves the dissolution of both additive and alloy particles and the competitive precipitation of γ_1, γ_2 and η' phases. These phases probably nucleate heterogeneously on impurity particles distributed throughout the liquid Hg solution [14, 15] and on the surfaces of the additive particles. Growth to impingement of the surface-nucleated crystals will produce continuous Asgar–Mahler reaction layers so that a second sintering stage ensues. This stage probably involves little or no further dissolution of Cu into the Hg solution [16] and is, therefore, characterized by the continuing precipitation of γ_1 and γ_2 in the bulk of the liquid and by growth of the reaction zones. An analysis of numerous TEM micrographs (e.g. Fig. 2a) has indicated that the volume fraction of the η' precipitate in the γ_1 matrix at 24 h is about $\frac{1}{50}$ of the η' volume fraction in the Asgar–Mahler zones. This result implies that the suppression of γ_2 precipitation by the preferential formation of η' largely takes place during the second sintering stage. Consequently, the overall efficiency with which a particular type of additive particle suppresses γ_2 precipitation is determined primarily by the gettering rate of Sn during growth of the reaction zones.

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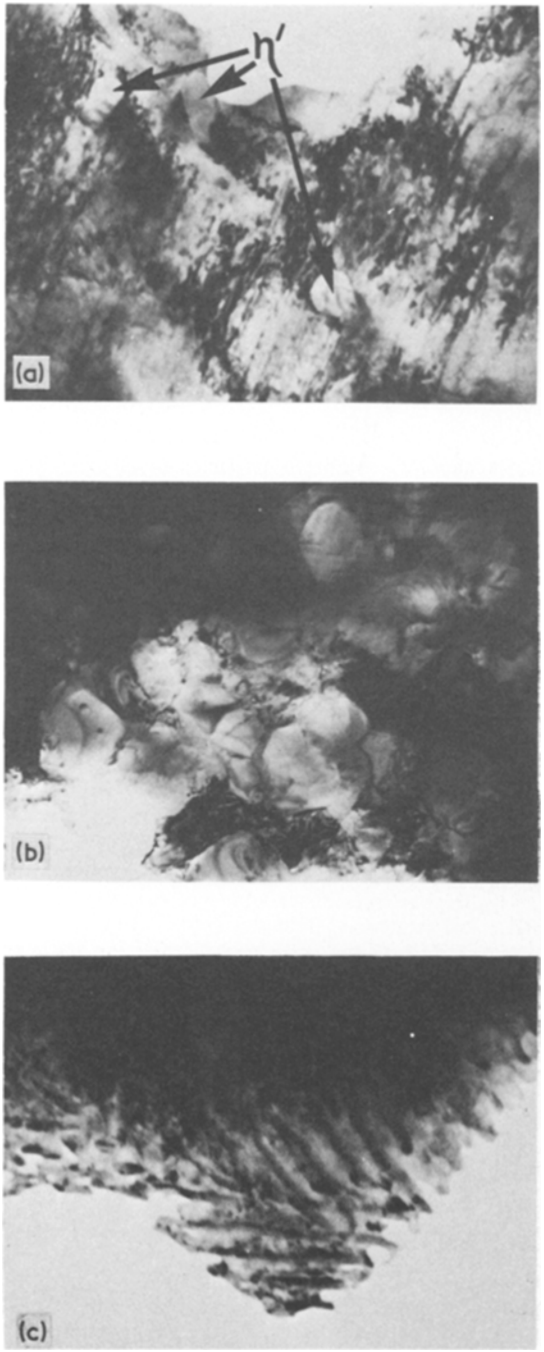

Figure 2 Transmission electronmicrographs of Dispersalloy amalgams prepared using the manufacturer's recommended procedures: (a) faulted γ_1 matrix grains containing small, rod-shaped η' precipitates; (b) fine-grained, microduplex structure of an Asgar–Mahler reaction layer; (c) lamellar structure of the eutectic Ag–Cu additive particles. Ion-beam thinned specimens, 200 kV acceleration voltage. (a) × 61 000, (b) × 34 000, (c) × 52 000.

The gettering efficiency of the atomized, eutectic particles in Dispersalloy have been determined by measuring the growth rate of the Asgar–Mahler zones for powder/Hg ratios of 1.5, 1.75 and 2.0. Measurements were made by first triturating weighed amounts of the Hg and the powder in a specially designed, low-energy amalgamator which gave sufficient agitation of the mix to suppress the development of concentration gradients in the liquid Hg solution. This solution was expressed at the end of trituration by condensing a small amount of the mix in a high pressure die. The resulting discs were quenched in liquid nitrogen before being fixed to a large, cold copper block by means of double-sided adhesive tape. Each of the discs was then polished, etched and examined optically. Repeated chilling of the block ensured that the condensed amalgam was kept as cold as was practicable in order to inhibit further growth of the zones. Icing during photomicrography was prevented by passing chilled, dry argon over the specimen surfaces. The elapsed time between condensation and photomicrography was restricted to times of 20 min or less in order to minimize any post-trituration growth of the reaction zones.

The true maximum width, w, of the zones for a given trituration time, t, was taken to be the maximum width of the reaction "haloes" observed around eutectic particles having the largest section diameter. Identification of the largest diameter was facilitated by sieving the as-supplied powder and using the fraction that passed through a 51 μm mesh.

It was found that growth of the zones could not be detected prior to an incubation time t_0, whereupon non-linear growth took place. The thickening data could be adequately described in terms of a parabolic equation of the form $w = K(t - t_0)^{1/2}$ where K is the parabolic rate constant. Furthermore, Fig. 3 shows that the data, when fitted in the least-squares sense to the parabolic rate law, fell to within the experimental accuracy on the same straight line for the three powder/Hg ratios. The slope of this line yielded $K = (1.5 \pm 0.2) \times 10^{-6}\,\mathrm{m\,sec}^{-1/2}$. Moreover, the incubation time was 2.7 min at the two highest powder/Hg ratios and it appeared to increase to 4.2 min as the ratio decreased to 1.5.

According to Wagner's [17] first-order theory

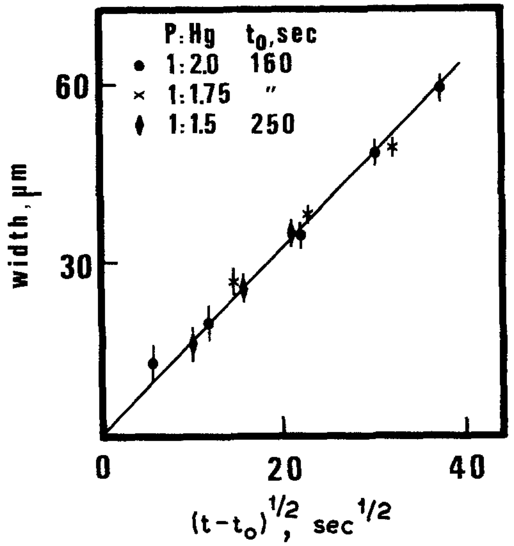

Figure 3 Parabolic growth kinetics of the Asgar–Mahler zones during the trituration of a sieved Dispersalloy powder.

for the parabolic growth of a reaction layer, $K \approx 2aD^{1/2}$ where D is the interdiffusion coefficient for the layer and a is a dimensionless constant satisfying an exponential-error function equation in the initial concentration, and in the concentrations at the surfaces of the layer. As a first approximation we can set $a \approx 0.5$ so that $D \approx 3.10^{-12}$ m^2 sec^{-1}. The volume diffusion coefficient of Ag in a predominantly γ_1 diffusion-couple layer is $\approx 10^{-15}$ m^2 sec^{-1} at 300 K [18] and the same coefficient for Sn in a predominantly γ_2 layer is $\leqslant 10^{-12}$ m^2 sec^{-1} at 300 K [18]. The comparatively large D value for growth of the Asgar–Mahler zones therefore suggests that growth involved short-circuiting diffusion via grain and interphase boundaries. If it is assumed that diffusion took place entirely at boundaries then the effective layer diffusivity is given by $D \approx 2D_b\delta/3d$ where D_b, δ and d are the average boundary diffusion coefficient, boundary thickness and grain size. For $d = 0.2\,\mu$m (see Fig. 2b) and assuming δ = 1 nm, the experimental parabolic rate constant for zone growth gives $D_b \approx 9.10^{-10}$ m^2 sec^{-1} at 300 K. This temperature corresponds to a normalized temperature T/T_m (where T_m is the melting point) of ≈ 1.25 for γ_1 and ≈ 2.0 for η' [19] so a weighted average for the reaction zones is ≈ 1.4. Reported [20] correlations between D_b and T_m/T indicate that $D_b \approx 10^{-10}$ m^2 sec^{-1} at $T_m/T = 1.4$. This inferred D_b compares favourably with the experimental value indicating that growth of the Asgar–Mahler zones was indeed controlled by boundary diffusion.

Since the rapid growth rate of the zones, and therefore the efficient gettering of Sn in Dispersalloy amalgams during the second stage of liquid-phase sintering, stems from the small grain size of the microduplex reaction zones, it is interesting to consider the factors that determine the grain size. Perhaps the most important variable is the scale of the segregation in the additive particles. The TEM micrograph of Fig. 2c shows that the additive particles in Dispersalloy typically contain a lamellar structure having an interlamellar spacing of 0.07 μm. It is tempting to speculate that this fine-scaled, regular structure promotes copious nucleation of the η' and γ_1 crystals during growth of the zones. This proposed relationship between the structure of the additive particles and the grain size (and growth rate) of the Asgar–Mahler zones may account for a portion of the large observed [21] variability of the efficiency of γ_2 suppression in dispersed-phase amalgam systems which form the zones.

It is perhaps relevant to point out that the factors promoting copious nucleation at the zone/eutectic interface during zone growth may also promote copious surface nucleation on the additive particle surfaces during the first sintering stage. Structure modifications leading to more efficient Sn gettering could therefore reduce the incubation time which is roughly equivalent to the duration of the first sintering stage. Any such reduction may serve to decrease the amount of η' that precipitates in the bulk of the liquid. This consideration could be important because, whereas large amounts of matrix η' (as in Sybralloy amalgams [22]) give a clinically undesirable decrease in toughness [23] and corrosion resistance [7], it is likely that a small volume fraction of suitably sized η' precipitates have the beneficial effects of reducing the creep rate and increasing the yield strength and wear resistance. The best strategy for manipulation of the structure of the additive particles would presumably be one which allows the independent control of the particle dissolution rate, the incubation time and the grain size of the reaction zones. It remains to be established whether the designers [3] of Dispersalloy have, perhaps inadvertantly, optimized the performance of the additive particles to give a suitable balance between the first stage precipitation of η' and the second stage gettering of Sn.

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Received 3 August
and accepted 20 September 1979

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Vickers micro-hardness of solid solution in the system Cr_2O_3–Al_2O_3

Aluminium oxide and chromium oxide form a continuous solid solution above 1000° C [1], and materials with a wide variety of properties are expected. In this communication, the Vickers micro-hardness was measured for the system Cr_2O_3–Al_2O_3 containing Cr_2O_3 up to 50 mol%.

Aluminium ammonium alum (Wako Junyaku, Reagent grade), chromium ammonium alum (Kanto Kagaku, Reagent grade) and magnesium sulphate (Wako Junyaku, Reagent grade) were used as starting materials. The specimens prepared are given in Table I. All specimens contained 0.7 mol% MgO as grain growth inhibitor. Weighed starting materials were mixed and heated in an alumina crucible at 550° C for 5 h, 950° C for 15 h and 1200° C for 3 h. The resultant oxide was pulverized for 1 h in an alumina ball mill. The formation of solid solution was confirmed by powder X-ray diffraction analysis ($CuK\alpha_1$, APD-10, Philips); the lattice parameters followed the Vegard's law. Rectangular bars (4 mm × 2 mm × 50 mm) were formed from the oxide powders at a pressure of $250\,\text{kg cm}^{-2}$ and pressed isostatically at $1000\,\text{kg cm}^{-2}$. They were buried in oxide powder of the same composition and sintered at 1600° C for 5 h in a water-saturated hydrogen stream or at 1700° C for 5 h in air. The apparent densities of sintered specimens were determined from their weights and dimensions. The specimens were buried in resin and their surfaces were polished with $\frac{1}{2}\,\mu$m diamond paste. The Vickers

0022–2461/80/051314–03$02.30/0