

CORROSION AND PASSIVITY BREAKDOWN OF HIGH COPPER DENTAL AMALGAMS

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Concerns with the toxicity of dental amalgams, especially with respect to marginal fracture, surface degradation, corrosion, release of corrosion products (particularly mercury) and biocompatibility have led to interest in the detailed mechanism of amalgam corrosion. Amalgams have been examined under different conditions similar to those encountered in the oral cavity - factors such as acidity, temperature and abrasion all influence the corrosion rate. It has been shown that a passivation layer formed on the amalgam surface significantly reduces the mercury release rate. Acids increase the corrosion rate and several studies varying pH have been undertaken. Nevertheless, the number of electrochemical studies of dental amalgams has been small.

Dental amalgams are formed by the reaction of mercury with a powder alloy containing mainly Ag, Sn, Cu and Zn, with other alloys in small concentrations. The product formed has a complex metallurgical structure which can contain up to six phases, each of which can contribute to the observed corrosion. These include intermetallic compounds of the tin-copper system, the matrix phase of the microstructure γ_1 -Ag₂Hg₃, γ -Ag₃Sn, γ_2 -Sn₇₋₈Hg, and the Ag-Cu eutectic (72% Ag, 28% Cu). Of these the matrix phase appears to be the most susceptible to corrosion. Spherical particles of the Ag-Cu eutectic are added to the alloy to increase the corrosion resistance by reducing the amount of γ_2 -Sn₇₋₈Hg.

The corrosion and electrochemical behaviour of individual amalgam phases has been investigated. The phases were prepared by mechanical amalgamation in the correct stoichiometric proportions and high pressure moulding, except for γ -Ag₃Sn which was prepared from molten liquid and tempered. The aggressivity of the oral cavity was simulated by 0.9% aqueous sodium chloride. Electrochemical measurements on the various phases were carried out using open circuit potential measurements, polarization curves, cyclic voltammetry and electrochemical impedance. Surface analysis has been carried out before and after corrosion takes place by optical microscopy and scanning electron microscopy.

Formation of a film of corrosion products on the surface of the phases occurs immediately after immersion, at the same time as the open circuit potential increases, reaching reasonably stable values after 1 h. Open circuit potential measurements and polarization curves show corrosion potentials most positive for γ_1 -Ag₂Hg₃, followed by γ -Ag₃Sn, Ag-Cu and γ_2 -Sn₇Hg, reflecting the order of corrosion resistance; corrosion currents follow the same trend. Electrochemical impedance measurements were carried out after 24, 48 and 72 hours immersion in the region near the open circuit potential, and were adjusted to equivalent circuits with good agreement. Since dental

amalgams are multiphase materials, complex spectra with diffusional components were obtained and evidenced differences in the corrosion mechanism and the extent of passivation. This is owing to the corrosion process being localised on defects in the non-homogeneous surface. The variation of the passive film thickness and corrosion rate was monitored.

Results obtained are compared with X-ray diffraction and scanning electron microscopy measurements and with those obtained for commercial dental amalgam.

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