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Corrosion of Dental Amalgams - Studies of Individual Phases

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Abstract. The corrosion resistance of commercial dental amalgam (Dispersalloy) and its component phases has been investigated. Electrochemical measurements were carried out in 0.9% NaCl which simulates the aggressivity of the oral cavity, using open circuit potential measurements, polarization curves and electrochemical impedance. The relative corrosion rates of the various phases, Ag-Cu, γ_1-Ag_2Hg_3, γ-Ag_3Sn and γ_2-Sn_7Hg was investigated as a function of immersion time using Tafel analysis of polarisation curves and impedance at the open circuit potential. Impedance measurements in the region of the open circuit potential led to complex spectra with diffusional components and showed differences in the corrosion mechanism between the phases. The microstructure of Dispersalloy, after potentiodynamic polarization, showed that the corrosion attacked the Ag-Cu eutectic particles and reaction zone surrounding the grain boundaries of the γ_1-phase at the surface of the amalgam.

Introduction

Amalgam is a metallic alloy formed by reaction between mercury and an alloy in powder form containing silver, tin, copper, zinc, etc. with a very complex metallurgical structure. Powder alloys can be classified into two groups: low copper content or conventional composition (5% or less copper) and high copper content (6 to 30% copper). Two different types of high copper alloy powders are available. The first is an admixed alloy powder and the second is a single-composition alloy powder [1].

On mixing, the mercury which dissolves in the silver-tin particles forms γ_1-Ag_2Hg_3 (the matrix phase in the microstructure) and γ_2-Sn_7Hg phases, leaving some unreacted γ-Ag_3Sn particles. In a relatively short time the newly formed γ_2-Sn_7Hg phase around the Ag-Cu eutectic (72% Ag, 28% Cu) reacts with silver-copper particles forming the η'-Cu_6Sn_5 phase of the copper-tin system along with some γ_1-Ag_2Hg_3 around the silver-copper particles.

Each of the different phases of the dental amalgam has a different corrosion potential and electrochemical behaviour. In the low-copper amalgam system, the phase most subject to corrosion is γ_2-Sn_7Hg [2]. Studies have shown that corrosion in chloride containing solution results in the formation of tin and the liberated mercury reacts with excess unreacted γ-Ag_3Sn (the second more prominent phase) [2]. It is proposed that the dissolution of the tin oxide or tin chloride formed results in porosity and lower strength [2,3].

The high-copper admixed and unicompositional alloys do not have any γ_2-Sn_7Hg phase in the final set mass. The η'-Cu_6Sn_5 phase formed in high-copper alloys is not an interconnected phase like the γ_2 phase, and is believed to have a better corrosion resistance. The γ-Ag_3Sn phase was considered to be electrochemically stable in the oral environment [2].

The corrosion of dental amalgam is thus a complex process, which involves contributions from each of the phases present as well as intergranular corrosion. It is thus of interest to investigate the corrosion of individual phases present in dental amalgams.

The corrosion resistance of commercial dental amalgam (Dispersalloy) and of its phases has been investigated by electrochemical measurements and carried out in 0.9% aqueous sodium chloride in order to simulate the aggressivity of the oral cavity.

Experimental

The alloy phases containing mercury were made in the correct stoichiometric proportions, taking into account the phase diagrams, by mechanical amalgamation and moulding under high pressure following the criteria adopted by the American Dental Association, Specification No. 1. The other alloys phases - γ-Ag_3Sn, Ag-Cu eutectic and η'-Cu_6Sn_5 - were prepared by heating the components until they were completely melted, and then the melt was poured into a mould to form an ingot. After the ingot was completely cooled, it was heated at 180ºC for one week (γ-Ag_3Sn and η'-Cu_6Sn_5) and at 770ºC for one week (Ag-Cu) and cooled slowly. The commercial dental amalgam employed was Dispersalloy, a copper-enriched alloy of the blended type: specimens were amalgamated following the manufacturer's instructions (Dentisply). All samples were examined by scanning electron microscopy and X-ray diffraction.

Electrodes were made by embedding samples in resin leaving one face exposed, area ~ 0.3 cm^2, polishing with 600 and 1000 grade emery papers, rinsing with distilled water and drying in air.

Electrochemical experiments were performed in a three-electrode cell containing 0.9% NaCl solution, an electrolyte similar to physiological serum. The counter electrode was Pt foil and the reference electrode was a saturated calomel electrode (SCE). Solutions were prepared using analytical grade reagent and Millipore Milli-Q water (resistivity > 18 MΩ cm), and were not deaerated. Experiments were carried out at room temperature (25±1ºC).

Open circuit corrosion potential and polarisation curve measurements were made with a EG&G PAR 273A potentiostat. Impedance measurements were carried out using a Solartron 1255 Frequency Response Analyser coupled to a Solartron 1287 Electrochemical Interface using a 10 mV rms perturbation in the frequency range 100 kHz to 0.1 Hz, 5 points per frequency decade, and controlled by ZPlot software; simulations were performed with ZView software. The impedance was measured after 24, 48 and 72 hours immersion at the open circuit potential.

Results

Scanning electron micrographs of Dispersalloy dental amalgam corroded in saline solution are shown in Fig.1, and has many phases and corrosion products.

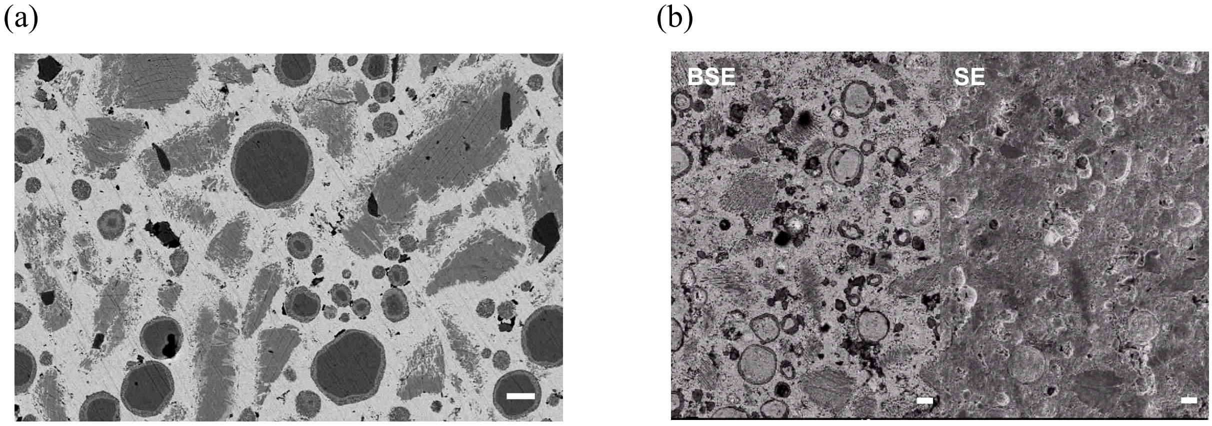

Fig.1- SEM of Dispersalloy: (a) surface before corrosion, (b) corroded surface after potentiodynamic polarization [-0.8 to +0.4V (SCE)]; left-backscattered electrons (BSE) and right-secondary electrons (SE). The dimension bars represent 10 μm.

The large, irregular particles are γ-Ag-Sn, with dark Cu-Sn areas within them. The round particles are Ag-Cu, with surrounding areas containing Ag-Hg and Cu-Sn phases. The matrix is Ag-Hg. The microstructure was identified by energy dispersive detection (EDAX) and revealed that Sn-containing corrosion products exist in many of the phases. After potentiodynamic polarization, the corrosion attacked the Ag-Cu eutectic particles and reaction zone surrounding the grain boundaries of the γ_1-phase at the surface of the amalgam. The various phases have also been examined by SEM.

The corrosion behaviour reflected by open circuit potential and polarisation potentiodynamic measurements has been examined in detail elsewhere [4,5]. Polarisation curves show corrosion potentials after short immersion times most positive for Ag-Cu, followed by γ_1-Ag_2Hg_3, and then significantly more negative for γ_1-Ag_3Sn and γ_2-Sn_7Hg. After 48h immersion the Ag-Cu potential becomes significantly more negative such that the most positive is γ_1-Ag_2Hg_3.

Table 1 Tafel analysis of polarisation curves for individual amalgam phases

Alloys	E_{cor} / mV *vs.* SCE		I_{cor} / μA cm^{-2}	
	10 min immersion	48 h immersion	10 min immersion	48 h immersion
Ag-Cu	-84	-222	39.0	50.6
γ_1-Ag_3Sn	-430	-337	10.6	13.8
γ_1-Ag_2Hg_3	-89	-118	18.2	12.3
γ_2-Sn_7Hg	-538	-526	1.6	40.6

Corrosion currents increase in all cases with the exception of the Ag-Hg phase, which shows a slight decrease. The difference in the trends between E_{cor} and I_{cor} between these binary phases demonstrates the interplay between rate-determining anodic (metal dissolution) and cathodic (oxygen reduction) reactions leading to surface oxide formation.

Electrochemical impedance spectra can throw further light on the interfacial processes occurring. Fig.2 shows the impedance spectra for Ag-Cu at applied potentials close to the corrosion potential.

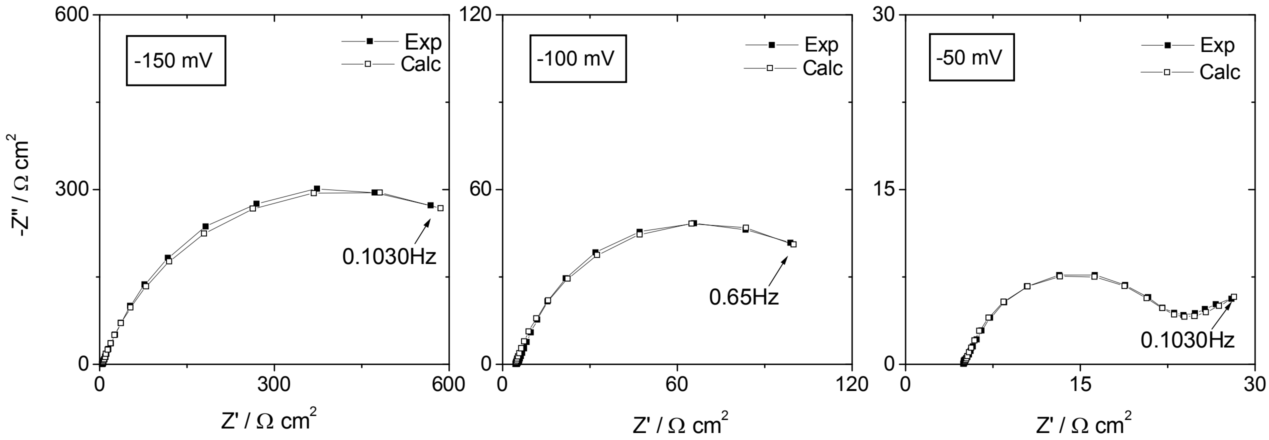

Fig.2 Complex plane impedance plots for Ag-Cu after 10 min immersion in 0.9% NaCl

The data were adjusted with an equivalent circuit consisting of a parallel combination of a resistance, R_1, and a Constant Phase Element (CPE), the CPE substituting the capacitance of the interfacial region up to –0.10 V *vs.* SCE. At –0.05 V *vs.* SCE a low-frequency diffusional component appears, showing the different nature of the corrosion process, requiring the introduction of a second CPE in series.

The impedance results for γ_1-Ag_2Hg_3 and γ_2-Sn_7Hg could be fitted at all potentials with the simpler circuit. On γ-Ag_3Sn a layer of corrosion products is formed partially or completely covering the surface of electrode; some of these products are probably SnO_2. This leads to different impedance spectra at applied potentials more positive than the corrosion potential (i.e. from –0.3 V): there is the appearance of two time constants and low frequency pseudo-inductive behaviour.

The impedance spectra recorded as a function of immersion time also demonstrate important changes for each phase, each of which requires individual treatment and will be reported elsewhere. Concerning the general behaviour, data obtained for Dispersalloy at the open circuit potential of ~0.l0 V vs. SCE show that after 24h immersion, the charge transfer semicircle, similar in form to that in Fig.2 but with higher impedance values (since Ag-Cu undergoes corrosion most readily), begins to disappear. The corrosion rate changes to a mixture of charge separation and diffusion occurring in the porous oxide layer formed at the metal-solution interface. This is shown by the low values of the CPE exponent, α, of around 0.65 as is also found for the individual phases.

Conclusions

Differences in the corrosion rates and mechanism for individual phases in Dispersalloy dental amalgams have been shown by electrochemical data. In Dispersalloy corrosion occurs in small spots, especially in irregularities such as voids and pores and attacks the Ag-Cu eutectic particles and reaction zone surrounding the grain boundaries of the γ_1-phase at the surface of the amalgam.

Corrosion potentials of individual phases after short immersion times are most positive for Ag-Cu, followed by γ_1-Ag_2Hg_3, and are significantly more negative for γ_1-Ag_3Sn and γ_2-Sn_7Hg. Corrosion currents follow a similar trend but the order changes after long immersion times, showing the importance of considering the anodic and the cathodic processes as rate-determining reactions.

Impedance spectra obtained for the individual phases show both charge transfer and diffusional components, according to the applied potential and the immersion time. Dispersalloy in saline solution showed enhanced distortion of the low frequency portion of the impedance curves and may be interpreted as involving non-uniform diffusion either in bulk or at the interface.

Future studies should take into account the influence of different bathing solutions and the effect of temperature.

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