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Determination of Light Elements in Amalgam Restorations

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Abstract

Rutherford backscattering has been used to measure the major elemental compositions in the near-surface regions of freshly prepared and used samples of dental amalgam. A depletion from bulk stoichiometry of the major elements, which indicates an accumulation of lighter elements on the surface of the materials, has been observed. Increases in the F, Na, Cl, P, O, C, and N concentrations between freshly prepared samples and used samples were measured by observation of gamma rays produced by proton and deuteron induced reactions.

Introduction

Corrosion potential has been correlated with clinical marginal failure¹ and creep² of dental amalgam. Specifically, the corrosion has long been associated with the attack of the tin component of the gamma-2 phase by chlorine and oxygen.³ Modern alloys have been developed in which gamma-2 phase production has been reduced. However, these improvements have not eliminated the corrosion¹ and subsequent failure of these alloys.⁴

In order to study corrosion, changes in the surface and near-surface composition of the amalgam need to be established, and nuclear analytical techniques can be utilized to assess these surface changes. Rutherford

backscattering⁵ is ideal for measuring the composition and depth distributions of the major heavy components such as Cu, Sn, Ag, and Hg in the first micrometer or so of the sample. Nuclear reaction analysis can be used to measure the quantity of light elements present at the surface. These techniques are unique in that multi-elemental analyses can be performed nondestructively with elemental sensitivities usually in the 1 to 1000 ppm range.

Four brands of dental amalgam were analyzed for changes in surface compositions due to use. The brands studied were Aristalloy CR, Dispersalloy, Optaloy II and Tytin. All of the samples had been catalogued as part of a continuing clinical study of the expected longevity of different alloys.⁶

Experimental

Eight samples of restorations from exfoliated deciduous teeth were obtained from five patients. All of the restorations had been in the mouth for between 2.5 and 4.5 years. Some of the samples were from the same patient. Patient #1 had restorations of Optaloy II and Tytin in the mouth for 3 years. Patient #3 had restorations of Dispersalloy and Optaloy II for 3.7 years, and Patient #5 had two restorations of Aristalloy CR in the mouth for 4.3 years. Each of these patients had both restorations placed within 4 weeks of the other. The subsequent exfoliations of both teeth were performed on the same day. The analyses were all performed on the proximal surface of each restoration.

The Brookhaven National Laboratory 3.5 MV Van de Graaff accelerator was used for the nuclear measurements. The Rutherford backscattering

measurements were made with a 2.9-MeV alpha particle beam which was elastically scattering at 165° and counted with a surface barrier detector. Processing of the amplified signals was accomplished with a Nuclear Data 6660 data acquisition system.

Light element analysis was performed using either a 3.5-MeV proton beam or a 2.5 MeV deuteron beam. The proton beam is useful for analyzing F, Na, Cl, and P through inelastic scattering. The deuteron beam is useful for analyzing C, O, and N through nuclear transformations. Characteristic gamma rays from the residual nuclei were counted at 90° with a Ge(Li) gamma-ray detector.

The absolute concentrations were determined by comparison with NBS Standard Reference Phosphate Rock (SRM 120B) for the F, Na, and P concentrations. The oxygen determination was made relative to Al_2O_3 and the carbon relative to graphite. Because of their apparent lower sensitivities, nitrogen and chlorine are more difficult to establish absolute concentrations; therefore, these results have presently been left as relative numbers.

As will be discussed in the next section, the results of the back-scattering show that a substantial gradient in at least some of the light element concentrations exists at the surface. This is in contrast to the reference materials, which are uniform in concentration. Therefore, the concentrations shown in Table I are not bulk concentrations, but are averaged over the concentrations in the near-surface regions of the samples. The range of 3.5-MeV protons in Dispersalloy is approximately 50 μm , and

the range of 2.5-MeV deuterons in Dispersalloy is approximately 22 μm . All of the gamma rays must be generated within these distances.

Results and Discussion

We previously reported⁷ the results of backscattering 2.9-MeV alpha particles from fresh and used samples of six amalgams: Caulk's Spherical, Cupraloy, Dispersalloy, Indiloy, Optaloy II and Tytin. Figure 1 shows backscatter spectra from freshly prepared and used samples of Tytin. Using the backscatter spectra, we were able to construct the near-surface concentrations of the major components of each amalgam. The energy difference between the mercury-scattering edge and the tin-scattering edge is 140 keV, which represents roughly the first 300 nm from the surface. The spectra from the used samples showed a rounding-off of each of the major elements' scattering edge. This rounding of edges indicates the surface of the sample had a substantial and non-uniform concentration of lighter elements. These lighter elements are maximum at the surface where the mercury is only 20% of its bulk concentration. At 300 nm into the sample, the mercury has reached its bulk concentration. These results prompted an effort to identify and measure the concentrations of these lighter elements by other nuclear techniques.

Proton inelastic scattering was used to measure the F, Na, Cl, and P concentrations in the amalgams, and Figure 2 shows a spectrum for 3.5-MeV protons incident on Dispersalloy. The peaks used for the analyses were the 197-keV ^{19}F , 439-keV ^{23}Na , 1.220-keV ^{35}Cl , and 1.266-keV ^{31}P gamma-ray peaks. The C, O, and N were measured with a deuteron beam

utilizing the $^{16}\text{O}(\text{d},\text{p})^{17}\text{O}$, $^{12}\text{C}(\text{d},\text{p})^{13}\text{C}$, and $^{14}\text{N}(\text{d},\alpha)^{12}\text{C}$ reactions.

Figure 3 shows a spectrum for 2.5-MeV deuterons incident on Dispersalloy.

The following gamma rays are identified: 0.87 MeV from ^{16}O ; 2.07 MeV, 3.09 MeV, and 3.67 MeV from ^{12}C ; and 4.43 MeV from ^{14}N .

Table I is a tabulation of the results of the nuclear reaction analysis. The lengths of time the samples were in the patients' mouths are included in this table. Concentrations of light elements from the used samples were compared to concentrations from samples of freshly prepared material. There were no measurable concentrations of F, Na, Cl, or P in the freshly prepared samples. There were only traces of carbon and nitrogen in the fresh samples and small measurable quantities of oxygen. The samples denoted with an "N" were the freshly prepared samples.

The Aristaloy CR and Optaloy II have been shown to have a higher incident of marginal breakdown than the Dispersalloy and Tytin.⁵ Since marginal breakdown is associated with corrosion, the differences in the concentrations of oxygen and chlorine should be important. The data in Table I show a significant amount of scatter in the concentrations. The Aristaloy CR and Optaloy II did show higher average chlorine concentrations than the Dispersalloy and Tytin. However, the Aristaloy CR sample G had the lowest concentration of Cl and Optaloy II sample C had one-half as much Cl as Dispersalloy sample F. Tytin was shown to have the smallest average oxygen concentration, and Optaloy II had the most, three times as much as the Tytin. Certainly the scatter in light element concentration is to be expected. This is illustrated in the spread in the

rate of marginal failures for each branch of amalgam as demonstrated by Nelson and Osborne.⁵

Since there is probably some patient dependence on the expected longevity of the samples, pairs of samples had been analyzed from the same patient. The most striking result of the chlorine concentrations is the order of magnitude difference between Aristalloy CR samples G and H, while there was only a factor of two difference (in the opposite direction) in the oxygen concentrations of these samples. The chlorine concentrations in samples Tytin A (Patient #1) and Optaloy II C (Patient #1) are virtually the same while sample C had four times as much oxygen as sample A. Sample Optaloy II D (Patient #3) had only slightly more oxygen than Dispersalloy F (Patient #3), but Optaloy II D had twice as much chlorine as Dispersalloy F.

Conclusions

Nuclear analytical techniques have been applied to the analysis of corrosion products on used samples of four brands of dental amalgams. The techniques have established the existence of use-induced concentration gradients of the amalgam components in the near-surface. The major components, Hg, Sn, Ag, and Cu become depleted, and the lighter elements become dominant. Thus far O, Cl, C, N, Na, F, and P have been identified as light elements that increase at the surface. However, concentration gradients of these particular elements have not been established. The concentration gradients of each element and its changes with time are important in the understanding of corrosion mechanisms.

The oxygen and chlorine action on the tin component of the gamma-2 phase has long been associated with corrosion. The results showed the presence of large quantities of oxygen and probably large quantities of chlorine. However, they also show substantial concentrations of carbon. These concentrations do not appear to be at insignificant levels and may indicate other corrosion processes.

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Table I. Composition of Light Elements in the Near-Surface Region of Dental Amalgams

Sample	O (at. %)	Cl (rel)	F (at. ppm)*	Na (at. ppm)*	P (at. ppm)*	C (at. %)	N (rel)
Tytin A Patient #1 3.0 years	4.2 ± .1	13 ± 3	67 ± 6	310 ± 45	1650 ± 110	10 ± 1	340 ± 15
Tytin B Patient #2 2.7 years	8.8 ± .2	8.3 ± 3	54 ± 6	160 ± 40	2600 ± 100	14 ± 1	380 ± 15
Opt II C Patient #1 3.0 years	18 ± 1	15 ± 3	32 ± 5	86 ± 39	1300 ± 100	17 ± 1	450 ± 15
Opt II D Patient #3 3.7 years	19 ± 1	71 ± 4	23 ± 5	900 ± 85	5800 ± 200	22 ± 1	680 ± 20
Disp E Patient #4 4.1 years	9.6 ± .2	8 ± 3	28 ± 6	570 ± 60	5300 ± 180	11 ± 1	310 ± 10
Disp F Patient #3 3.8 years	11 ± 1	35 ± 4	24 ± 5	900 ± 80	4300 ± 200	17 ± 1	430 ± 15
Aris G Patient #5 4.3 years	14 ± 1	7 ± 5	5 ± 4	87 ± 14	310 ± 130	33 ± 2	840 ± 20
Aris H Patient #5 4.3 years	7.3 ± .5	68 ± 9	220 ± 20	270 ± 25	8200 ± 360	4 ± 1	99 ± 9
Tytin N	.35 ± .05					Trace	Trace
Opt IIN	.19 ± .05					Trace	Trace
Disp N	1.2 ± .1					Trace	Trace
Aris N	.4 ± .05					Trace	Trace

* atomic parts per million

Figure 1. Backscatter spectra from 2.9-MeV alpha particles incident on freshly prepared and used samples of Tytin.

Figure 2. Gamma-ray spectrum from 3.5-MeV protons incident on used Dispersalloy.

Figure 3. Gamma-ray spectrum from 2.5-MeV deuterons incident on used Dispersalloy.