Project Title: Effect of Localized Corrosion on Dental Amalgams

Project No: E-19-B04 (Continuation of E-19-B03)

Project Director: Dr. M. Marek

Sponsor: DHEW/PHS/National Institute of Dental Research

Agreement Period: From 6/1/79 Until 5/31/81

Type Agreement: Grant No. 2R01 DE0 3601-07

Amount: $41,844 (PHS, E-19-B04) $4,993 (GIT, E-19-344) $46,837 TOTAL

Reports Required: Interim Progress Report; Terminal Progress Report

Sponsor Contact Person(s):

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Defense Priority Rating: n/a

Assigned to: Chemical Engineering (School/Laboratory)

COPIES TO:

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Other
GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT TERMINATION

Date: June 10, 1980

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Project No: E-19-B04

Project Director: Dr. M. Marek

Sponsor: DHEW/PHS/National Institute of Dental Research

Effective Termination Date: 6/30/80

Clearance of Accounting Charges: 6/30/80

Grant/Contract Closeout Actions Remaining:

- Final Invoice and Closing Documents
- Final Fiscal Report (Interim)
- Final Report of Inventions (Interim)
- Govt. Property Inventory & Related Certificate
- Classified Material Certificate
- Other

CONTINUED BY E-19-B05

Assigned to: Chemical Engineering (School/Laboratory)

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CA-4 (1/79)
EFFECT OF CORROSION ON DENTAL AMALGAMS

1. List publications: (a) published and not previously reported; (b) in press. Provide five reprints if not previously submitted.
2. List all additions and deletions in professional personnel and any changes in effort.
3. Progress Report. (See Instructions)

Publications

Changes
Effort: No Change
Personnel: Dr. Steven Reese, postdoctoral trainee, participated in one part of the program (no salary compensation).

Progress Report

OBJECTIVES
A. Overall Objectives
To improve the understanding of the role of corrosion in the deterioration of dental amalgam restorations by investigating the mechanism of corrosion, the effects of corrosion on the properties, and by developing suitable testing methods.

B. Goals For The Current Year
a. To investigate the mechanism of corrosion of high copper dental amalgam.
b. To investigate the relationship between creep and corrosion of dental amalgam.
c. To initiate a study of the relationship between porosity, mercury content and corrosion of dental amalgam.
d. To evaluate the corrosion test based on controlled potential coulometry.

2. STUDIES AND RESULTS
a. A Study of the Mechanism of Corrosion of High Copper Dental Amalgam

Earlier studies have shown that in the corrosion affected zone copper is depleted, the Cu₆Sn₅ deteriorates, and some of the γ₁ phase changes into β₁. In this study the reactions and the mass transport have been examined. In one part of the study the electrolyte (1% NaCl) in which specimens were actively corroding was analyzed periodically by atomic absorption spectrophotometry for metallic ions, and solid corrosion products were analyzed by electron microprobe. The results show that initially tin dissolves but solubility is quickly reached and the main product of the reaction are insoluble tin compounds, mainly tin oxychloride. Copper enters the solution later but the release rate soon exceeds that of copper. Some solid copper corrosion products (chloride) were also found. Since the amalgams did not contain the tin-rich γ₂ phase it is thought that the tin initially originates in the γ₁ phase; this destabilizes the phase and facilitates the transformation into β₁. Copper is released when the Cu₆Sn₅ phase breaks down and is trans-
ported by diffusion to the surface where it dissolves. Further tests are planned to test this hypothesis.

The transport of copper through the matrix phases was investigated. Samples of \( \gamma_1 \) and \( \beta_1 \) phases were prepared, electroplated with copper, maintained at constant temperature, sectioned, and analyzed by electron microprobe. The results, reported to the 1980 Annual Session of the AADR (1) show that copper diffused about two times faster in the \( \beta_1 \) than in the \( \gamma_1 \) phase. The diffusion parameters were determined. Thus the \( \gamma_1 - \beta_1 \) transformation facilitates the transport and the corrosion process.

b. A Study of the Relationship Between Creep and Corrosion

Mahler and other investigators have shown that creep correlates well with the incidence of marginal breakdown of amalgam restorations. A recent joint study (2) has shown that both creep and corrosion depend similarly on some variables. In the first part of this study the effect of tin and zinc contents on the creep of the \( \gamma_1 \) and \( \beta_1 \) phases was examined. Specimens of both phases with systematically varied zinc and tin contents were prepared and tested for ADA creep. The results, presented to the 1980 Annual Session of the AADR (3), show that \( \beta_1 \) creeps much more slowly than \( \gamma_1 \); tin increases sharply creep of both phases; zinc decreases creep of the \( \gamma_1 \) phase but has little effect on \( \beta_1 \); some combinations of tin and zinc results in embrittlement of the matrix. The same specimens used in the creep study are now tested for the corrosion resistance.

The Principal Investigator also participated in a study of the creep of corroded dental amalgam conducted at the Medical College of Georgia. The corroded amalgams showed lower creep indicating that corrosion results in the loss of plasticity (4).

c. A Study of the Effect of Porosity on Corrosion of Dental Amalgam

The study was initiated in the current year. Specimens of a conventional amalgam were prepared and the nominal surface was determined from the dimensions. The actual total surface area was then determined by measuring the adsorption and desorption isotherms at low temperature using Krypton gas. The results show that the actual total surface area, which includes the surface area of the open pores, was about twenty times higher than the nominal area. This demonstrated the very important role of porosity in the corrosion processes. The surface area determination technique will be used in the continuation of this study.

d. Evaluation of the Corrosion Test

The corrosion test based on constant potential coulometry (5) has been used in several phases of this program and the data have been collected for statistical analysis. A study was made of the basic processes involved in the test. Specimens were tested using different exposure times and the relationship between the anodic charge and the corrosion depth has been determined. Examination of the micro-structural changes is in progress.

e. A Study of the Galvanic Interactions Between Dental Amalgam and Other Restorative Materials

This study was conducted in addition to the planned program in view of the important galvanic effects observed in the previous part of the project. In one part of the study the interaction between metals which are not in contact was analyzed theoretically and examined experimentally. In the second part the interactions between metals in contact were measured using two dental amalgams (conventional and high copper) and dental casting alloys which included high-gold, low-gold, silver-palladium, and base-metal alloys. The results, presented to the 1980 Annual Session of the AADR (6), can be summarized as follows: 1. There is no significant interaction between dissimilar metals in the mouth which are not in contact; 2. There is a substantial concentration macrocell due to the difference...
between saliva and the tissue fluids, which may have an important effect on the
corrosion of the part of the restoration within the tooth cavity; 3. The measure-
ment of open circuit potential differences between various dental materials is of
little value in predicting the intensity of the galvanic interactions.

References:
1. S. Reese, R. F. Hochman, and M. Marek: "Low Temperature Diffusion of Copper
in the γ₁ and β₁ Phase of Dental Amalgam". Annual Session of the AADR, March
2. M. Marek and D. B. Mahler: "The Corrosion Susceptibility of a High Copper
Amalgam as a Function of the Mercury Content". Annual Session of the AADR
and the 57th General Session of the IADR, March 29 - April 1, 1979, New Orleans,
Paper No. 968.
as a Function of Composition". Annual Session of the AADR, March 20-23, 1980,
Los Angeles, Paper No. 105.
of a Corroded High Copper Amalgam", ibid., Paper No. 282.
6. M. Marek: "Galvanic Interactions Between Dental Amalgam and Other Restorative
Materials". Annual Session of the AADR, March 20-23, 1980, Los Angeles,
Paper No. 1033.

3. SIGNIFICANCE
The proposed research will contribute to the understanding of the basic
processes of deterioration of dental amalgam restorations and thus help in the
development of improved materials.

4. RESEARCH GOALS FOR THE COMING YEAR
a. A Study of the Mechanism of Corrosion of High Copper Amalgam: To inves-
tigate the breakdown of the Cu₆Sn₅ phase by metallographic examination
and microanalysis of specially prepared samples simulating the amalgam
microstructure.

b. A Study of the Relationship Between Mechanical Properties and Corrosion:
To complete the determination of the effects of composition on the corrosion
of the matrix phases (to complement the creep tests) and to determine the
effect of simultaneous creep and corrosion.

c. A Study of the Relationship Between Porosity and Corrosion: To determine
the above relationship for one dental amalgam using the techniques of
surface area determinations developed in the current year.

d. Evaluation of the Electrolytes Used in the In vitro Corrosion Tests: To
determine the data unavailable in the literature for the test media used
todate (pH, buffering capacity, redox potential).

The undersigned agrees to accept responsibility for the scientific and technical
conduct of the project and for provision of required progress reports if a grant is
awarded as the result of this application.

4/21/80
Date

Principal Investigator