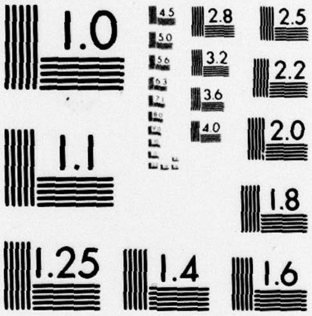
AD-A080 949 ARMY INST OF DENTAL RESEARCH WASHINGTON DC F/G 6/5
ELECTROCHEMICAL PROFILES OF CROWN-AND-BRIDGE ALLOYS,(U)
FEB 80 E F HUGET, S G VERMILYEA, F A MODAWAR

UNCLASSIFIED NL

1 OF 1
AD-
A080949

END
DATE
FILMED
2-80
DDC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

12

LEVEL II

ADA080949

## REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

| | | |
|---|---|---|
| 1. REPORT NUMBER | 2. GOVT ACCESSION NO. | 3. RECIPIENT'S CATALOG NUMBER |
| 4. TITLE (and Subtitle)<br>6<br>Electrochemical Profiles of Crown-and-Bridge Alloys | | 5. TYPE OF REPORT & PERIOD COVERED<br>Manuscript |
| | | 6. PERFORMING ORG. REPORT NUMBER |
| 7. AUTHOR(s)<br>10<br>[redacted] Eugene F. Huget [redacted] Stanley G. Vermilyea<br>[redacted] Faris A. Modawar [redacted] James J. Tamura | | 8. CONTRACT OR GRANT NUMBER(s) |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>U.S. Army Institute of Dental Research<br>Walter Reed Army Medical Center<br>Washington, D.C. 20012 | | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS<br>OG 6044<br>00-369-1 |
| 11. CONTROLLING OFFICE NAME AND ADDRESS<br>U.S. Army Medical Research and Development Command<br>ATTN: (SGRD-RP) Fort Detrick, Maryland 21701 | 11 | 12. REPORT DATE<br>11 Feb[redacted]80 |
| | | 13. NUMBER OF PAGES<br>12 |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)<br>12 12 | | 15. SECURITY CLASS. (of this report)<br>Unclassified |
| | | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE |

16. DISTRIBUTION STATEMENT (of this Report)

Unlimited

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

DTIC
ELECTE
S FEB 2 1 1980 D
B

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

[illegible]

DDC FILE COPY

18. SUPPLEMENTARY NOTES

Military Medicine

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Crown and bridge alloys; low gold alloys; electrochemical behavior of low gold alloys and corrosion of low gold alloys.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The resistance of four crown-and-bridge alloys to halide attack was assessed. In aerated medium, the equilibrium behavior of two gold containing alloys was characterized by passivity, whereas that of two materials of lesser nobility was typified by active dissolution.

Corrosion rates of the test alloys were accelerated in oxygen depleted medium. In deaerated solvent, the passive equilibrium condition was experienced only by a nickel-chromium based alloy.

80 2 21 005

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

038670 JM

# ELECTROCHEMICAL PROFILES OF CROWN-AND-BRIDGE ALLOYS

COL Eugene F. Huget*
LTC Stanley G. Vermilyea+
SP/5 Faris A. Modawar**
SP/5 James J. Tamura**

U.S. Army Institute of Dental Research
Division of Dental Materials
Washington, D.C. 20012

* Chief, Division of Dental Materials

\+ Research Dental Officer

** Physical Scientist

# ELECTROCHEMICAL PROFILES OF CROWN-AND-BRIDGE ALLOYS

Continued escalation of the cost of gold has prompted growing interest in the fabrication of fixed dental prostheses from a wide variety of medium gold, low gold, silver-palladium and base metal alloys. Accordingly, the importance of preclinical assessment of the abilities of the so-called alternative alloys to resist destructive dissolution and tarnish has been recognized.[1-3]

The present investigation was conducted to establish and to compare the corrosion behavior patterns of four castable materials marketed as alternatives to high gold content alloys.

## Materials and Methods

Materials subjected to *in vitro* testing included a gold (49%)-palladium (31%) alloy,[*] a palladium (40%)-gold (20%) alloy,[+] a silver (71%)-palladium (25%) alloy,[#] and a nickel (76%)-chromium (12%) alloy.[§]

Specimens were cast from each material through the use of conventional lost wax dental laboratory procedures. Each casting was a 1-mm X 12-mm rod with an enlarged rhomboidal end. The specimens, except those cast from the silver-palladium based alloy (Cast All) were heat treated by exposure to a

---

[*] Neydium (Gold Ceramic Alloy), The J. M. Ney Co., Hartford, CN 06101.

[+] P-G (Porcelain Gold), American Gold Co., Los Angeles, CA 90004.

[#] Cast All, Leff Dental Golds Inc., Woodside, NY 11377.

[§] Biobond (Ceramic Bonding Alloy), Dentsply International Inc., York, PA 17404.

simulated porcelain firing cycle.[¶]

The cylindrical segment of each casting was polished with 240- to 600-grit abrasive papers, cleansed in detergent, rinsed with ethanol and air dried. The rhombic portion of each piece was inserted into the split end of a 6-mm diameter copper tube. Continuity of the tube-specimen connection was maintained by a force-fitted and wax-sealed Teflon sleeve.

A halide medium (solvent) exhibiting a chloride ion concentration comparable to that of pooled human saliva[4] was prepared by dilution of 1 part by volume lactated Ringer's solution[**] (chloride ion conc. 109 m Eq/L)

---

¶ (1) Degassing: Specimens were heated from 1,200° to 1,950°F, held at 1,950°F for 5 minutes, removed from the furnace, and cooled in open air. (2) Simulated application of opaque porcelain: Specimens were heated from 1,200° to 1,825°F, removed from the furnace immediately on reaching 1,825°F, and cooled to room temperature in open air. (3) Simulated application of body porcelain: Specimens were subjected to two successive firings from 1,200° to 1,775°F. Specimens were cooled to room temperature in open air after each firing. (4) Simulated application of glaze: Specimens were heated from 1,200° to 1,800°F, removed from the furnace immediately on reaching 1,800°F, and cooled to room temperature in open air.

** Cutter Laboratories, Inc., Berkeley, CA 94710.

with 4.5 parts by volume deionized water. Prior to use, 500 ml aliquots of medium for one series of electrochemical experiments were allowed to stand undisturbed in a 1-liter capacity open corrosion cell for 1 hour. Medium conditioned in this manner was considered aerated. Temperature of the aerated medium was maintained at 37±2C. Deaeration of chloride solvent for subsequent experiments was accomplished by allowing air-free nitrogen to diffuse through 500 ml aliquots of freshly diluted stock Ringer's solution for a period of 1 hour. Then the terminus of the nitrogen delivery device was withdrawn from the solution and positioned to allow continuous coverage of the surface of the liquid medium with a protective blanket of inert gas. Temperature of the deaerated medium was maintained at 37±2C.

Upon completion of the medium conditioning procedure, the copper tube-specimen assembly (potentiostat-specimen connector) was lowered into the corrosion cell to a depth that allowed complete immersion of the cylindrical segment of the casting. The polarization cycle was initiated at -1.0V versus a saturated calomel electrode (SCE) by application of a potential of -1.0V to the counter electrode of the corrosion cell. Each specimen (working electrode) was polarized anodically at a rate of 0.01V per sec with the use of a programmable potentiostat.[++] Polarization was allowed to proceed anodically until an increase in current density of approximately 3 decades was experienced by the working electrode. Then the direction of change

---

[++] Universal Programmer, Model 175, Analytical Instrument Division, Princeton Applied Research Corp., Princeton, NJ 08540.

of the impressed potential was reversed. Completion of the polarization cycle was marked by return of the specimen to a potential of -1.0V versus SCE.

Output of the potentiostat was monitored continuously on a Cartesian coordinate recorder.[##] Graphic displays of changing current density with impressed potential produced anodic and cathodic potentiodynamic polarization diagrams.

The salient features of a cyclic polarization diagram are presented in the figure. Cathodic protection existing at the onset of polarization is depicted by broken line AB. Anodic behavior is denoted by solid line BE which yields coordinate values for oxidation (zero current) potential (B), primary passive potential and critical current density (C) and breakdown potential (D). An abrupt decrease in anodic current density resulting from scan direction reversal is shown by solid line segment EF. Onset of cathodic reduction (zero current) potential is marked by point F. The reduction phase of the cyclic schematic is illustrated by the broken lines emanating from the latter point. Corrosion (equilibrium) potential,[a] as defined in terms of modern mixed potential electrochemical theory, is marked by intersection of the cathodic reduction and anodic dissolution curves.

---

[##] X-Y Recorder, Model 9002A, Analytical Instrument Division, Princeton Applied Research Corp., Princeton, NJ 08540.

[a] Potential at which oxidation and reduction of an alloy occur at equal rates.

Locations of the intersections of cathodic curves FG, FH and FI with the anodic curve reflect equilibrium conditions of activity,[b] passivity[c] and transpassivity,[d] respectively.

## Results

Data obtained on polarization of the test materials in aerated medium are given in Table 1. Oxidation of Neydium, PG, Cast All and Biobond began at potentials negative to that of the reference electrode. Current densities of the same order of magnitude were experienced by all four alloys at the onset of passivation. Neydium exhibited the most noble primary passive, breakdown and reduction (zero current) potentials, whereas PG exhibited the most noble equilibrium potential. The equilibrium potential of Cast All was slightly anodic to its breakdown potential. The most active primary passive, breakdown and equilibrium potentials were shown by Biobond. Neither Cast All nor Biobond were passive at equilibrium.

Data summarizing the responses of the crown-and-bridge alloys to polarization in deaerated medium are presented in Table 2. Deaeration reduced the effectiveness of impressed cathodic protection. Oxidation (zero current) and primary passive potentials were significantly more active than those observed on polarization of the test materials in aerated medium. Current density required for passivation of Neydium and PG tended to be an order of

---

[b] Vigorous attack of solute (alloy) by solvent (medium).

[c] Solute protected by a stable oxide film from further attack by solvent.

[d] Breakdown of solute's protective film and continued solute-solvent interaction.

magnitude higher than that required for passivation of the alloys of lesser nobility. PG exhibited the most noble breakdown and reduction (zero current) potentials. Additionally, PG was at equilibrium with the deaerated solvent at impressed potentials of +70 mv (transpassive), -110 mv (passive) and -540 mv (active). Neydium and Cast All were transpassive at respective equilibrium potentials of -50 and +50 mv. Biobond was passive at its equilibrium potential of -750 mv.

## Discussion

Understandably, caution must be exercised in the extrapolation of laboratory findings to clinical experience. The data, however, point out marked differences that exist among the electrochemical profiles of crown-and-bridge alloys. These differences reflect variations in the abilities of the alloys to passivate spontaneously and thereby resist halide attack.

In aerated halide medium, oxygen competes with chloride ions for adsorption sites on the solute alloy. Hence, the oxidizing power of the halide constituent is reduced. In the presence of sufficient amounts of oxygen, equilibria of the redox reactions of Neydium and PG favor maintenance of stable oxygen-rich passive films at potentials intermediate to the alloys' primary passive and breakdown potentials. On the other hand, the loosely adherent oxygen-rich films formed on anodic polarization of Biobond undergo complete reduction on cathodic polarization. Equilibrium of the redox reaction is attained at a potential cathodic to the primary passive potential of the alloy.

In contrast to the foregoing, the oxidizing power of chloride ions is increased by deaeration of the halide medium. Corrosion rates, as indicated by current density-impressed potential relationships are accelerated in oxygen-depleted solvent. It would appear that such conditions are required for the spontaneous passivation of Biobond and other alloys of exceedingly low nobility.

The complex corrosion profile obtained on cyclic polarization of PG in deaerated medium may be a manifestation of the multiphasic structure of low gold-high palladium-high silver alloys. It is likely that the passive surfaces of restorations cast from alloys exhibiting multiple equilibrium potentials could be rendered permanently active by abrading their protective films.

The behavior of Cast All in both aerated and deaerated media is compatible with the disparity that exists between the nobility of silver and the nobility of palladium. At relatively cathodic potentials, silver is attacked vigorously by the test solvents, whereas palladium is not. Palladium, the more noble element creates a mixed potential within the alloy's transpassive region and a correspondingly high corrosion rate.

## Summary

The resistance of four crown-and-bridge alloys to halide attack was assessed. In aerated medium, the equilibrium behavior of two gold containing alloys was characterized by passivity, whereas that of two materials of lesser nobility was typified by active dissolution.

Corrosion rates of the test alloys were accelerated in oxygen depleted medium. In deaerated solvent, the passive equilibrium condition was experienced only by a nickel-chromium based alloy.

## TABLE 1

## ELECTROCHEMICAL PROFILES OF CROWN-AND-BRIDGE ALLOYS

| | Aerated Medium<br>Alloys | | | |
|---|---|---|---|---|
| Observations | Neydium | PG | Cast All | Biobond |
| Activation (Zero current) Potential, mv vs SCE | -110 | -290 | -150 | -640 |
| Primary Passive Potential, mv vs SCE | -50 | -190 | -80 | -550 |
| Critical Current Density, ma/cm$^2$ | 8.0X10$^{-3}$ | 6.0X10$^{-3}$ | 5.0X10$^{-3}$ | 9.0X10$^{-3}$ |
| Breakdown Potential, mv vs SCE | +300 | +200 | +50 | -240 |
| Reduction (Zero current) Potential, mv vs SCE | +450 | +400 | +270 | -150 |
| Equilibrium (Corrosion) Potential, mv vs SCE | -30 | +120 | +60 | -580 |
| Equilibrium Condition | Passive | Passive | Transpassive | Active |

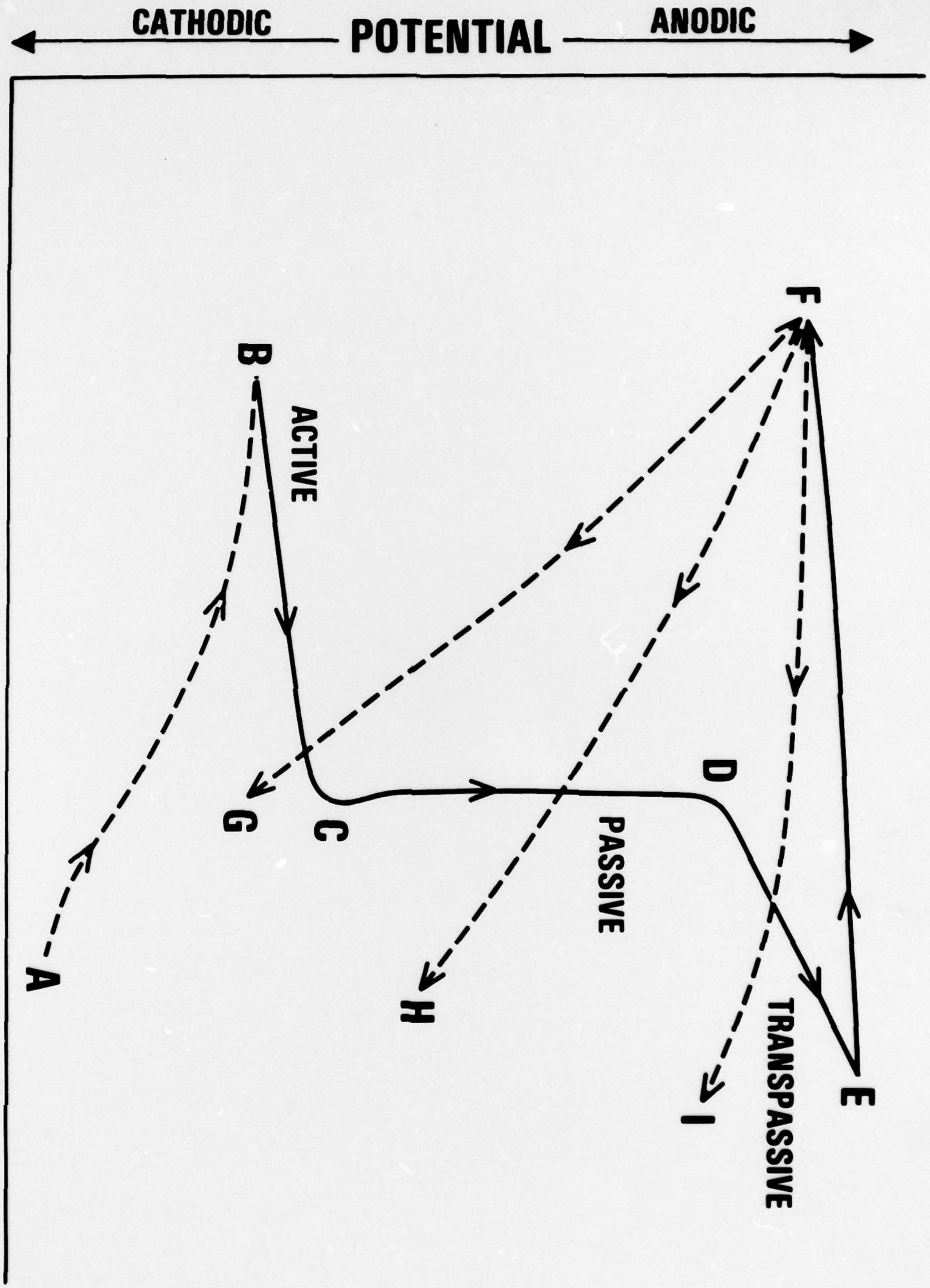
## TABLE 2

## ELECTROCHEMICAL PROFILES OF CROWN-AND-BRIDGE ALLOYS

| | Deaerated Medium | | | |
|---|---|---|---|---|
| | Alloys | | | |
| Observations | Neydium | PG | Cast All | Biobond |
| Activation (Zero current) Potential, mv vs SCE | -700 | -600 | -280 | -900 |
| Primary Passive Potential, mv vs SCE | -450 | -350 | -200 | -820 |
| Critical Current Density, ma/cm$^2$ | $1.0 \times 10^{-2}$ | $3.5 \times 10^{-2}$ | $5.0 \times 10^{-3}$ | $6.0 \times 10^{-3}$ |
| Breakdown Potential, mv vs SCE | -250 | +50 | +20 | -650 |
| Reduction (Zero current) Potential, mv vs SCE | -390 | +460 | +270 | -40 |
| Equilibrium (Corrosion) Potential, mv vs SCE | -50 | +70<br>-110<br>-540 | +50 | -750 |
| Equilibrium Condition | Transpassive | Transpassive<br>Passive<br>Active | Transpassive | Passive |

## Legend for Figure

Schematic cyclic potentiodynamic polarization curves.


CATHODIC
POTENTIAL
ANODIC
CURRENT DENSITY
A
B
ACTIVE
C
G
D
PASSIVE
H
E
F
I
TRANSPASSIVE