Dissolution rate of cadmium from dental gold solder alloys

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The dissolution rate of cadmium from six different dental gold solder alloys was determined in an *in vitro* potentiostatic study. The measurements were made in the potential range 740—880 mV and attempts have been made to extrapolate the results to a potential region that might in reality occur in the oral cavity. For comparison the dissolution rates of copper and zinc were also determined. Electrochemically the most interesting quantity was the logarithm of the dissolution rate because it is a linear function of the applied potential. This linear relationship was given by the Tafel equation. The dissolution rate of cadmium was shown to be rather small even under circumstances which may be said to represent very unfavourable conditions within the oral cavity.

Key-words: Gold alloys; cadmium

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Corrosion problems associated with the use of dental metal restorations have been studied for many years (*Lain et al.*, 1940; *Schoonover & Souder*, 1941; *Schriever & Diamond*, 1952; *Stegemann*, 1956; *Swartz et al.*, 1958; *Frykholm et al.*, 1968, 1969; *Maschinski*, 1970). Conventional test methods for corrosion are not sufficiently sensitive and cannot be adapted easily to the measurement of the corrosion rate *in vivo*. The lack of a satisfactory test suited to *in vivo* studies of corrosion has lead to the development of various laboratory tests. Measurements have been made of dissimilar alloys which are used in the oral cavity in direct and in intermittent contact.

In dental practice at least two alloys are connected in soldered bridgeworks. Previous studies (*Hedegård*, 1958; *Bergman & Björnham*, 1972) have demonstrated that corrosion damage to this type of restoration is most likely to occur in the regions of the soldered joints. The fact that the soldering has in many cases to be carried out step-by-step or has sometimes to be partly redone has made it necessary to use gold solder alloys of different melting ranges. Among these gold solder alloys the lower-fusing types very often contain cadmium as an alloy element.

As this metal can be enriched and stored for a long period in various tissues of the mammalian body, especially in the liver and kidney (*Friberg*, 1950; *Berlin & Ullberg*, 1963; *Friberg & Piscator*, 1972; *Bergman et al.*, 1975), it would be of great interest to determine the corrosion behaviour of dental alloys containing cadmium. As new electrochemical methods are now available for corrosion studies *in vitro* there has recently been increased

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interest in this field (*Ross et al.*, 1967; *Guthrow et al.*, 1967; *Brugirard et al.*, 1973; *Sarkar & Greener*, 1973). *Brugirard et al.* (1973) studied the electrochemical behaviour of some dental gold alloys. They found that zinc and cadmium were the alloy elements most liable to corrosion, followed to a lesser degree by copper.

In most studies of this type the conclusions are based mainly on the relationship between the electric current and the potential during the progress of the corrosion experiment. However, this current is a very complex quantity which is difficult to interpret because it is the result of a number of chemical reactions. In the present work a specific reaction has been studied by means of direct chemical analysis of the solution after the corrosion experiment.

The purpose of the present study thus was to determine *in vitro* the dissolution rate of cadmium from commercial dental gold solder alloys of those types which are commonly used in soldered bridge constructions. For comparison the dissolution rates of copper and zinc were determined.

The measurements were made in the potential range 740—880 mV versus SCE and attempts have been made to extrapolate the results to a region of between 500 and 600 mV (*cf* Fig. 4). In this region some of the greatest observed potential values versus a fixed reference electrode have been found *in vivo* (*Maschinsky*, 1970).

MATERIAL AND METHODS

Specimen preparation. The alloy materials in the form of thin bands (cross section 0.3 mm × 1.0 mm) were taken from different batches bought on the open market. The sample band was mounted in a glass tube as shown in Fig. 1. The tube was then sealed with Canada balsam. The exposed surface of the alloy was about 2—4 cm².

Fig. 1. Specimen mounting. The sample band was coiled and mounted in a glass tube.

The compositions of the alloys, as concerns the alloy elements studied in the present work, are given in Tables II—IV. The analyses were performed by Analytica AB, Sollentuna, Stockholm. »Analysis 1» was made by the roentgen fluorescence method on alloy samples with the same marking as the electrode specimens. Before this analysis was performed the material was melted. »Analysis 2» was made by atomic absorption spectrophotometry on the residues of the electrodes after the corrosion experiments. In this case the samples were directly dissolved in acid.

Electrolyte. The electrolyte used was physiologic saline (isotonic sodium chloride solution for infusion). By the addition of 0,01 M potassium hydrogen phtalate the pH of the solution was buffered to 4.0. This electrolyte solution was marked »A». In human saliva pH varies from 5.8 to 7.6, commonly 6.4—7.1. Thus pH = 4 is well below the normal values which can be found in saliva.

However, in connection with a supply of sugar the pH value of dental plaque deposits may fall to about 4.5 for a short period.

The value of pH = 4.0 was thus chosen to create more unfavourable conditions than are likely to be present at the soldered joints of dental gold bridges. Furthermore the dissolved metal will not withdraw from the chemical analysis due to hydroxide precipitation. In one test series the same physiological saline solution (with 0.01 M potassium hydrogen phtalate) was used but pH was adjusted to 6.5 with sodium hydroxide solution. The latter electrolyte solution was marked »B».

According to *Hoar & Mears* (1966) inorganic solutions are satisfactory substitutes for extracellular body fluids, at least when the anodic behaviour of passive metals is under consideration.

Artificial saliva was not used in this study in order to avoid the presumed risk of formation of complex ions which would make the interpretation of the results much more intricate. Plasma or body fluid consists of an aerated solution containing approximately 1 percent sodium chloride, together with minor amounts of other salts and organic compounds, and thus a physiologic saline solution was chosen as the electrolyte. The concentrations of Cd, Cu and Zn in this electrolyte were < 0.1 ppm, < 0.1 ppm and 0.1 ppm respectively, as determined by atomic absorption spectrophotometry.

The gas phase consisted of an oxygen-nitrogen mixture of known composition (0.209 ± 0.005 % O_2), purchased from Alfax AB, Malmö. Thus in the experiments the partial pressure of the oxygen was 0.2 kPa as compared to 21 kPa in normal air. Oxygen interferes with the metal dissolution. It is practically impossible to remove all oxygen and the composition chosen was judged to give well defined experimental conditions. The gas was bubbled through the solution which was thereby also continuously agitated. The experiments were performed at room temperature.

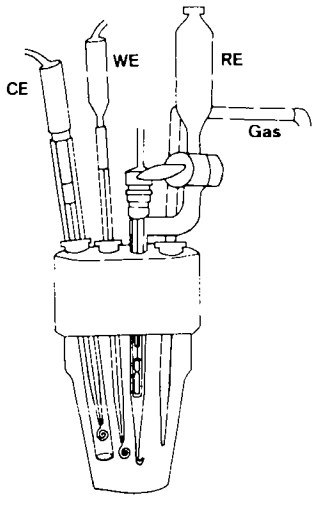

Fig. 2. The measuring cell. Legend: CE = counter electrode; WE = working electrode (the specimen); RE = reference electrode; Gas = gas inlet tube.

Electrochemical measurements. The electrochemical cell is shown in Fig. 2. The basis for the construction was the cover which had five holes with standard bore NS 14. In the holes the various electrodes and the gas inlet and outlet tubes were mounted using NS 14 polypropylene stoppers. The beaker was fastened to the cover with a thread and contained 50 ml of the electrolyte.

The working electrode, WE, consisted of the sample. The current direction was anodic (metals were dissolved):

$$Me(s) \rightarrow Me^{2+} + 2e^{-}.$$

The counter electrode, CE, consisted of a spiral of platinum wire mounted in a 10 mm glass tubing with a plug of glass filter at the bottom. The electrolysis current passed through the solution and

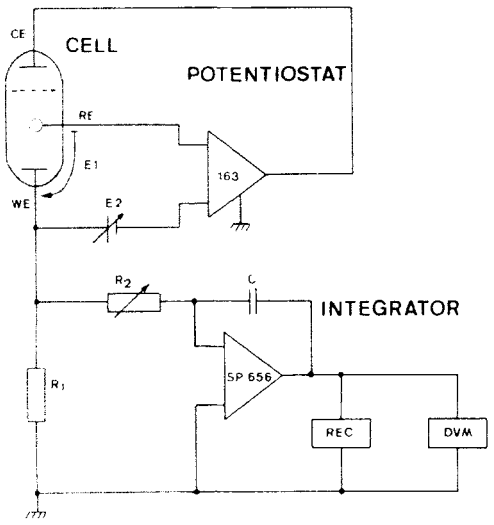

Fig. 3. Principal schematic diagram of the cell, potentiostat and integrator. Legend: CE, WE and RE are the electrodes as in Fig. 2; E1 = potential difference between RE and WE; E2 = adjustable control voltage; 163 = operational amplifier, Analog devices 163; R1 = precision resistor, 10.68Ω; R2 = precision switchable resistors, 200 kΩ, 2 MΩ or 20 MΩ; C = polystyrene precision condenser, 5.0 μF; SP656 = chopper stabilized operational amplifier, Philbrick SP656; REC = strip chart recorder, HEATH JR-18 M; DVM = digital voltmeter.

the glass filter and evolved hydrogen gas at the counter electrode:

$$2H^+ + 2e^- \rightarrow H_2(g).$$

The hydrogen gas escaped through small holes in the upper part of the glass tubing. The glass filter prevented the hydrogen gas from reaching the working electrode, where it could interfere with the metal dissolution.

The reference electrode, RE, was a commercial saturated calomel electrode (Metrohm AG, CH-9100 Herisau). The electrolytic contact with the solution was in the tapered and belled tip, thus convection and diffusion of the saturated potassium chloride solution was avoided. Several reference electrodes were compared. They agreed within a few millivolts.

The potentiostat, Fig. 3, sensed the potential difference between the working electrode and the reference electrode. This potential difference was compared with a preset voltage from a ten-turn potentiometer, E2. The action of the potentiostat was to send an appropriate electrolysis current through the counter and working electrode system to bring the potential difference E 1 close to the preset voltage, E2. The tolerance was a fraction of a millivolt. The common value of E1 and E2 is denoted by E in the following.

The electrolysis current was integrated by means of an electronic integrator. The integrator reading was taken from a digital voltmeter and from a recorder (scan rate 1 inch/20 min). The electronic components were adjusted to give a direct reading of the amount of electricity, Q, passing the working electrode (unit used: micromoles of electrons, μ mol e^-). The accuracy of the adjustment was better than 0.1 %. The experimental setup was similar to that described by *Johansson* (1965). The controlled potential coulometric principle is further elucidated in *Lingane's* textbook (1958).

A measurement was performed as follows: with breaking of the electrolysis circuit the cell was mounted, the electrolyte solution filled, the system de-aired for some time and the integrator was set at zero. The electrolysis was started and the current integral was recorded. When an appropriate amount of electricity had reacted (commonly 30 μ mol e^-) the experiment was terminated and the solution was analysed with respect to Cd, Cu and Zn by atomic absorption spectrophotometry (Department of Analytical Chemistry, University of Umeå, Sweden).

Calculations. The primary results of the present study are collected in Table I.

Table I. *Primary results. »E vs SCE» denotes the potential of the metal specimen in relation to saturated calomel electrode. —— Q is the quantity of electricity. Concentrations given are analytical values. —— »Current efficiency» is defined as* $2 \cdot \frac{n_{Me}}{n_{e^-}}$ *where* n_{Me} *is the amount of dissolved metal and* n_{e^-} *is the amount of electrons that have passed the electrode-solution interface. The numeral 2 takes into account that the actual metal ions have the charge 2. —— »Dissolution rate» is the amount of dissolved metal per unit time and unit electrode area (unit: mol* $s^{-1}m^{-2}$*). —— LDR = log (Dissolution rate). -- The electrolyte solution A was used throughout except in the experiments with specimen code 1. —— Column 2—8 are measured primary values and are given with the experimentally obtained precision.*

Specimen code	Electrode area mm²	E vs SCE mV	Q µmol e⁻	Time min	Concentrations of the three metals in the solution Cd ppm	Cu ppm	Zn ppm	Current efficiency for dissolution of the three metals Cd	Cu	Zn	Sum (Cd+Cu+Zn)	Logarithm of the dissolution rate of the three metals Cd	Cu	Zn
1	416	880	30.00	20	2.15	4.2	0.25	0.06	0.22	0.01	0.29	-6.72	-5.18	-6.42
1	416	840	30.00	95	2.95	5.0	0.35	0.09	0.26	0.02	0.37	-6.26	-5.78	-6.95
1	416	760	8.19	2470	1.40	2.2	0.30	0.15	0.42	0.05	0.62	-8.00	-7.55	-8.43
1	416	800	16.45	440	2.0	3.2	0.35	0.11	0.31	0.03	0.45	-7.09	-6.64	-7.61
2	406	880	30.00	15	3.8	5.9	0.70	0.11	0.31	0.04	0.46	-5.33	-4.90	-5.83
2	406	840	30.00	30	3.8	6.0	0.65	0.11	0.31	0.03	0.45	-5.64	-5.19	-6.17
2	406	800	29.70	110	4.5	6.2	0.70	0.13	0.33	0.04	0.50	-6.13	-5.74	-6.70
2	406	760	13.13	1690	2.6	3.7	0.45	0.18	0.44	0.05	0.67	-7.55	-7.15	-8.08
10	402	880	30.00	15	0.70	10.0	3.6	0.02	0.52	0.18	0.72	-6.07	-4.66	-5.12
10	402	840	30.00	30	0.65	9.2	3.3	0.02	0.48	0.17	0.67	-6.40	-5.00	-5.46
10	402	800	30.00	105	0.65	9.5	3.5	0.02	0.50	0.18	0.70	-6.94	-5.53	-5.98
10	402	760	13.09	245	0.40	9.6	1.6	0.03	1.15	0.19	1.37	-7.52	-5.89	-6.68
10	402	740	29.45	2485	0.85	12.3	4.9	0.03	0.66	0.25	0.94	-8.20	-6.79	-7.20
10	402	760	19.64	445	0.50	7.2	2.4	0.02	0.58	0.19	0.79	-7.68	-6.28	-6.77
10	402	800	30.00	100	0.65	9.6	3.5	0.02	0.50	0.18	0.70	-6.92	-5.50	-5.95
10	402	840	30.00	30	0.65	10.0	3.6	0.02	0.52	0.18	0.72	-6.40	-4.96	-5.42
10	402	880	30.00	15	0.65	10.2	3.8	0.02	0.54	0.19	0.75	-6.10	-4.65	-5.10
11	390	880	30.00	10	9.0	6.7	0.55	0.27	0.35	0.03	0.65	-4.77	-4.65	-5.75
11	390	840	30.00	20	9.0	6.7	0.50	0.27	0.35	0.03	0.65	-5.07	-4.95	-6.09
11	370	800	30.00	80	9.0	6.7	0.55	0.27	0.35	0.03	0.65	-5.65	-5.53	-6.63
11	370	760	24.58	1700	8.9	6.4	0.50	0.32	0.41	0.03	0.76	-6.98	-6.87	-7.99
11	370	800	30.00	75	9.0	6.5	0.55	0.27	0.34	0.03	0.64	-5.62	-5.51	-6.60
11	370	840	30.00	20	9.0	6.7	0.55	0.27	0.35	0.03	0.65	-5.04	-4.93	-6.02
11	370	880	30.00	10	9.0	6.7	0.50	0.27	0.35	0.03	0.65	-4.74	-4.62	-5.76
11	370	760	24.90	1605	9.0	7.0	0.55	0.32	0.44	0.03	0.79	-6.95	-6.81	-7.93
9	192	800	26.80	230	6.5	6.1	1.30	0.22	0.36	0.07	0.65	-5.96	-5.74	-6.43
9	192	880	30.00	20	7.0	6.8	1.35	0.21	0.36	0.07	0.64	-4.87	-4.63	-5.35
9	192	840	30.00	45	5.5	6.2	1.25	0.16	0.33	0.06	0.55	-5.53	-5.03	-5.73
9	192	820	30.00	90	6.0	6.4	1.30	0.18	0.34	0.07	0.59	-5.59	-5.31	-6.02
9	192	780	23.96	450	5.0	5.6	1.15	0.19	0.37	0.07	0.63	-6.37	-6.07	-6.77
3	420	880	30.00	10	8.5	6.4	0.55	0.25	0.34	0.03	0.62	-4.62	-4.70	-5.78
3	420	840	30.00	20	8.5	6.4	0.55	0.25	0.34	0.03	0.62	-5.12	-5.00	-6.08
3	420	800	30.00	80	8.5	6.5	0.55	0.25	0.34	0.03	0.62	-5.73	-5.60	-6.68
3	420	860	33.00	15	9.5	7.0	0.55	0.26	0.33	0.03	0.62	-4.95	-4.84	-5.95
3	420	880	30.00	10	8.5	6.3	0.55	0.25	0.33	0.03	0.61	-4.82	-4.71	-5.78
3	420	800	30.90	90	8.5	6.6	0.55	0.24	0.34	0.03	0.61	-5.78	-5.64	-6.73
3	420	780	15.95	100	5.0	3.6	0.40	0.28	0.35	0.04	0.67	-6.05	-5.95	-6.92
3	420	740	31.82	120	9.5	5.4	0.65	0.27	0.27	0.03	0.57	-5.85	-5.85	-6.78
4	176	880	283.2	275	64	60	5.8	0.20	0.33	0.03	0.56	-5.01	-4.79	-5.82
4	176	840	190.3	450	44	40	5.0	0.21	0.33	0.04	0.58	-5.39	-5.18	-6.09
4	176	800	108.4	1405	24	20	2.7	0.20	0.29	0.04	0.53	-6.14	-5.97	-6.86
4	176	840	350.4	1050	80	72	9.9	0.20	0.32	0.04	0.56	-5.49	-5.29	-6.17
4	176	880	300.0	290	65	60	8.1	0.19	0.31	0.04	0.54	-5.02	-4.81	-5.69
5	372	840	222.1	435	26	44	3.0	0.10	0.31	0.02	0.43	-5.92	-5.45	-6.63
5	372	800	50.00	1260	10	14	1.5	0.18	0.44	0.05	0.67	-6.80	-6.41	-7.39
5	372	800	273.8	2395	44	56	6.1	0.14	0.32	0.03	0.49	-6.44	-6.08	-7.06
5	372	880	268.8	130	44	54	6.1	0.15	0.32	0.03	0.50	-5.17	-4.83	-5.79
6	230	800	3.00	40	1.2	1.0	0.3	0.35	0.52	0.15	1.02	-6.01	-5.85	-6.38
6	230	780	3.00	125	0.2	0.6	0.1	0.06	0.31	0.05	0.42	-7.29	-6.56	-7.35
6	230	760	4.73	1195	0.3	1.0	0.1	0.05	0.33	0.03	0.41	-8.09	-7.32	-8.33
6	230	800	3.00	70	0.2	0.5	0.1	0.06	0.26	0.05	0.37	-7.04	-6.39	-7.10
6	230	800	3.00	45	0.2	0.5	0.1	0.06	0.26	0.05	0.37	-6.84	-6.20	-6.91
6	230	820	3.30	20	0.2	0.6	0.1	0.05	0.28	0.05	0.38	-6.49	-5.77	-6.56
6	230	840	3.00	10	0.2	0.5	0.1	0.06	0.26	0.05	0.37	-6.19	-5.54	-6.26
6	230	860	3.00	5	0.3	0.6	0.1	0.09	0.31	0.05	0.45	-5.71	-5.16	-5.96
6	230	880	3.00	5	0.3	0.6	0.1	0.09	0.31	0.05	0.45	-5.71	-5.16	-5.96
6	230	760	4.99	995	0.5	1.0	0.1	0.09	0.31	0.03	0.43	-7.79	-7.24	-8.25
6	230	780	3.00	90	0.2	0.6	0.1	0.06	0.31	0.05	0.42	-7.14	-6.42	-7.21
6	230	800	3.00	25	0.3	0.6	0.1	0.09	0.31	0.05	0.45	-6.41	-5.86	-6.65
12	410	800	30.00	110	9.0	4.9	0.2	0.27	0.26	0.01	0.54	-5.83	-5.85	-7.25
12	230	820	30.78	75	9.0	4.9	0.3	0.26	0.25	0.01	0.52	-5.41	-5.43	-6.65
12	230	840	30.00	40	9.0	4.9	0.3	0.27	0.26	0.02	0.55	-5.14	-5.16	-6.38
12	230	860	30.00	25	9.0	4.9	0.4	0.27	0.26	0.02	0.55	-4.94	-4.95	-6.05
12	230	880	30.56	15	9.0	4.9	0.4	0.26	0.25	0.02	0.53	-4.71	-4.73	-5.83
12	230	840	30.00	35	9.0	4.9	0.4	0.27	0.26	0.02	0.55	-5.08	-5.10	-6.20
12	230	760	11.80	2290	6.0	2.9	0.4	0.45	0.39	0.05	0.89	-7.07	-7.14	-8.01

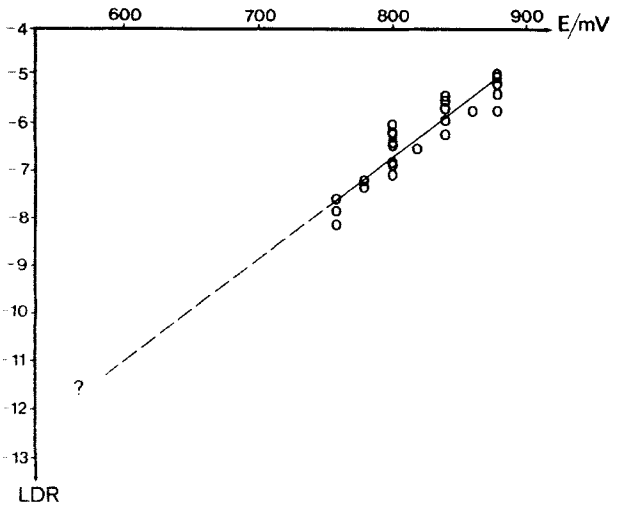

Fig. 4. The logarithm of the dissolution rate (*LDR*) as a function of the applied potential (*E*). The least squares straight line describing the measuring points will be extrapolated to a potential range (500—600 mV) which can be found in the oral cavity.

Columns 2—8 contain measured quantities whereas the last 7 columns contain calculated quantities, first current efficiencies and then logarithms of dissolution rates. The current efficiency is defined in the text of Table I. It is the fraction of the amount of electricity used for the dissolution of one of the metals. If there were no reactions other than the dissolution of Cd, Cu and Zn, the sum of the current efficiencies of these three metals would amount to unity.

Electrochemically the most interesting quantity is the logarithm of the dissolution rate, defined in the text of Table I. This quantity is denoted by *LDR*. In the present investigation the measurements are centered around $LDR = -6$. This corresponds to a dissolution rate of 10^{-6} mol s^{-1} m^{-2} or a dissolution rate of 3.5 mg Cd $year^{-1}$ mm^{-2} or a current density of 20 μA cm^{-2} (only the fraction of the current depending on dissolution of the actual metal).

The reason for using the logarithmic scale for the dissolution rate is evident from Fig. 4. *LDR* is a linear function of the applied potential E. According to electrode kinetic theory (*Vetter*, 1967) the following relationship may be expected

$$\eta = a + b \log i \qquad (1)$$

(Tafels equation) where η is the overtension (departure of the actual potential from the equilibrium value), i is the electrolysis current and a and b are constants. In our particular case, Tafels equation may be formulated:

$$LDR = C1 + C2(E - 800 \text{ mV}) \qquad (2)$$

where *C1* and *C2* are constants, referring to the measuring series and 800 mV is a potential value chosen arbitrarily in the center of the measuring range.

The measuring points of each measuring series have been fitted to equation (2) by means of a least squares computer program. The results are to be seen in Table II (cadmium), Table III (copper) and Table IV (zinc). In Table II, the *LDR* for cadmium has been extrapolated to $E = 550$ mV.

RESULTS

The sum of the current efficiencies for the dissolution of the three metals is considerably less than unity (with two exceptions,

Table II. *Final results for Cd. In the column »weight per cent» the figures denote analysis values of the alloys in question. —— Solution A = physiological saline solution with 0.01 M potassium hydrogen phtalate added; pH = 4.0. Solution B = physiological saline solution with 0.01 M potassium hydrogen phtalate added; pH adjusted to 6.5 with sodium hydroxide solution. —— LDR = log (Dissolution rate); see the text to Table I. —— C1 and C2 are constants, refering to the measuring series. —— The ranges indicated are 95 % confidence intervals.*

Material					Tafel equation					
Specimen Code	Commercial name	Weight per cent Cd Analysis 1	Analysis 2	Solution	[The least squares straight line $LDR = C1 + C2(E-800\ mV)$] *Equation*	*Standard deviations* $C1$	$C2 \cdot 10^3$ / mV^{-1}	LDR	LDR extrapolated to $E = 550$ mV Value*	S.D.
1	JS 730	6.97	12.5	B	$LDR = -7.2 + 19 \cdot 10^{-3}mV^{-1}(E-800\ mV)$	0.3	7	0.14	—11.9	1.8
2, 4, 5, 6	JS 730	6.97	9.53—12.0	A	$LDR = -6.7 + 20 \cdot 10^{-3}mV^{-1}(E-800\ mV)$	0.2	4	0.36	—11.6	1.0
10	Degulor 2	0.7	0.81	A	$LDR = -7.1 + 14 \cdot 10^{-3}mV^{-1}(E-800\ mV)$	0.1	3	0.17	—10.6	0.7
9	ANA 2	0.1	9.2	A	$LDR = -6.0 + 15 \cdot 10^{-3}mV^{-1}(E-800\ mV)$	0.1	4	0.09	— 9.7	1.1
3	Protor 1	9.3	12.9	A	$LDR = -5.6 + 9 \cdot 10^{-3}mV^{-1}(E-800\ mV)$	0.2	4	0.20	— 8.0	1.0
12	Degulor 1	11.7	12.7	A	$LDR = -6.0 + 19 \cdot 10^{-3}mV^{-1}(E-800\ mV)$	0.3	6	0.23	—10.8	2.5
11	Protor 2	13.7	15.3	A	$LDR = -6.0 + 18 \cdot 10^{-3}mV^{-1}(E-800\ mV)$	0.3	6	0.30	—10.5	1.6

Table III. *Final results for Cu.* For details see text to Table II.

Material					Tafel equation			
Specimen Code	Commercial name	Weight per cent Cu Analysis 1	Analysis 2	Solution	[The least squares straight line $LDR = C1 + C2(E-800\ mV)$] *Equation*	*Standard deviations* $C1$	$C2 \cdot 10^3$ / mV^{-1}	LDR
1	JS 730	12.2	9.90	B	$LDR = -6.7 + 20 \cdot 10^{-3}mV^{-1}(E-800\ mV)$	0.3	5	0.12
2, 4, 5, 6	JS 730	12.2	9.63—10.4	A	$LDR = -6.2 + 18 \cdot 10^{-3}mV^{-1}(E-800\ mV)$	0.1	3	0.24
10	Degulor 2	21.9	21.1	A	$LDR = -5.6 + 14 \cdot 10^{-3}mV^{-1}(E-800\ mV)$	0.2	3	0.20
9	ANA 2	12.3	11.9	A	$LDR = -5.7 + 15 \cdot 10^{-3}mV^{-1}(E-800\ mV)$	0.2	4	0.11
3	Protor 1	11.9	8.97	A	$LDR = -5.5 + 10 \cdot 10^{-3}mV^{-1}(E-800\ mV)$	0.2	3	0.17
12	Degulor 1	9.6	8.63	A	$LDR = -6.0 + 20 \cdot 10^{-3}mV^{-1}(E-800\ mV)$	0.3	6	0.24
11	Protor 2	13.0	11.5	A	$LDR = -5.8 + 18 \cdot 10^{-3}mV^{-1}(E-800\ mV)$	0.3	6	0.30

* Any deviation of these values from those received from the Tafel equations given in the table is due to the number of decimals used in the original material.

Table IV. *Final results for Zn.* For details see text to Table II.

Specimen Code	Material: Commercial name	Material: Weight per cent Zn, Analysis 1	Material: Weight per cent Zn, Analysis 2	Solution	Tafel equation: [The least squares straight line $LDR = C1 + C2(E - 800\ mV)$] *Equation*	*Standard deviations* $C1$	*Standard deviations* $C2 \cdot 10^3$ / mV^{-1}	*Standard deviations* *LDR*
1	JS 730	1.31	1.43	B	$LDR = -7.7 + 17 \cdot 10^{-3}mV^{-1}(E - 800\ mV)$	0.2	5	0.10
2, 4, 5, 6	JS 730	1.31	1.39—1.44	A	$LDR = -7.1 + 18 \cdot 10^{-3}mV^{-1}(E - 800\ mV)$	0.1	3	0.30
10	Degulor 2	5.6	5.56	A	$LDR = -6.1 + 15 \cdot 10^{-3}mV^{-1}(E - 800\ mV)$	0.2	2	0.15
9	ANA 2	7.1	1.94	A	$LDR = -6.4 + 14 \cdot 10^{-3}mV^{-1}(E - 800\ mV)$	0.2	5	0.11
3	Protor 1	0.93	1.43	A	$LDR = -6.5 + 9 \cdot 10^{-3}mV^{-1}(E - 800\ mV)$	0.2	3	0.18
12	Degulor 1	0.76	0.87	A	$LDR = -7.2 + 19 \cdot 10^{-3}mV^{-1}(E - 800\ mV)$	0.2	4	0.15
11	Protor 2	0.83	0.86	A	$LDR = -7.0 + 18 \cdot 10^{-3}mV^{-1}(E - 800\ mV)$	0.3	6	0.31

which might be due to some error). This indicates that there might be other metals dissolving simultaneously.

The material called »JS 730» was used in five measuring series (with specimen codes 1, 2, 4, 5 and 6). The four measuring series with specimen codes 2, 4, 5 and 6 are merely reproductions with different specimen samples and as these four measurement series gave no significantly different results they were all treated together to yield a common linear *LDR*-E relationship for each metal (See Tables II—IV).

The measuring series with the »JS 730», specimen code 1, was performed in solution B (pH = 6.5) in contrast to all the other measuring series, where solution A (pH = 4.0) was used. A comparison of the first two lines in Tables II—IV shows that the slopes are unaffected by pH, but the *LDR* values at $E = 800$ mV are significantly lower in solution B. The constancy of the slopes indicates that the mechanisms of the electrode reactions are unaffected by pH. The change in the *LDR* values indicates that the dissolution is slower when the solution is less acid, possibly as a result of oxide film formation. This means that the results obtained in solution A are to be regarded as the worst case results, as the pH in the region of a solder hardly goes down to 4.0.

In testing materials 4 and 5 the quantity of electricity used was about ten times larger, and for material 6 about ten times smaller, than the quantity used for the rest of the material. This variation in the quantity of electricity does not seem to affect the results. This fact indicates that from this point of view the prehistory of the single electrode does not influence to any great extent the results of the present study. Comparable values for the amount of dissolved metal per unit of time and surface are in good agreement.

When the metal content of the alloys is compared with *LDR* at $E = 800$ mV it is found that a low metal content also gives a low dissolution rate (see Tables II—IV). However, the variations are quite large and are probably due to metallurgical variables.

DISCUSSION

Corrosion is an attack on a material through chemical or electrochemical reaction with the surrounding medium. As the varying and complex oral milieu under biological conditions can hardly be reproduced under laboratory conditions the interest has been focused on the evaluation of adequate test methods for *in vitro* tests of the corrosion behaviour of dental alloys. The clarifying of the electrochemical reactions involved in corrosion of a dental gold alloy in a well defined environment thus contributes to an understanding and evaluation of the corrosion effects *in vivo* (*Burse et al.*, 1972).

The specimens of the gold solder alloys used as electrode materials in the present work were not melted before the experiments started but were used as bands as they were delivered. The concentrations of the different alloy elements given in Tables II—IV which were obtained from roentgen fluorescence analysis (Analysis 1) was obtained from the same alloys after a preceding melting of the materials. According to certain manufacturers of these and similar alloys about half of the original cadmium content disappears by evaporation during the melting process. This statement could be confirmed as regards one of the alloys studied in the present work. In this case the analysis value for the Cd-content could be compared to the known amount of Cd which was added to the alloy during the manufacturing process. A partial evaporation of the Cd-content during melting means that the dental technician who solders dental bridgework runs the risk of inhaling the Cd-vapour. As inhaled Cd is absorbed to a much larger extent than ingested Cd (*Friberg et al.*, 1971) this aspect must be taken into consideration when choosing solder alloys containing Cd.

As the alloys for the electrode materials in the present study were bought from different batches it is not possible to say with any certainty that the percentual amounts given in Tables II—IV and gained from »Analysis 1» correspond to the compositions on which the final results are based. According to the representatives of the manufacturers in question the composition of alloy materials 9 and 10 has been changed in that the Cd content has been reduced from about 9 weight per cent to almost zero. This measure was probably taken because in 1974 the Swedish National Board of Health and Welfare (MF 1974: 34) issued a statement which contained definite advise against the use of dental gold alloys containing cadmium.

In an attempt to clarify the actual conditions as regards the contents of cadmium, copper and zinc the residues of all the electrodes were analysed using atomic absorption spectrophotometry. This method does not involve any melting of the material but is in the present case less accurate than roentgen fluorescence analysis. However, the latter method demands a larger amount of material than the available electrode residues. Thus any melting of the material before the analysis should be born in mind when, for example, differing values for the cadmium content are obtained from the two analytical methods. These values are collected in Tables II—IV.

It can be seen from Tables II and IV that for the alloy materials 9 and 10 a low cadmium content is associated with a high zinc content. Thus the decreased amount of cadmium was compensated for by an increased amount of zinc to avoid drastic changes in the fusion temperature of the solder alloy. These two metals are fairly similar in character as regards chemical attack although cadmium is a little more resistant.

The fact that the dissolution rate of the alloy elements studied was not proportional to the amount of the metal in question indicates that other factors influencing the process must be taken into consideration. Metallurgical variables may change the free energy of the electrode material and, for a given metal, alter its position in the galvanic series. From this point of view the most important of such variables are high energy grain boundaries, presence of different phases, residual internal energy resulting from cold working of the material, compositional and surface heterogeneities and foreign inclusions.

In single phase metals and alloys the grain boundaries because of their greater stored energies are anodic to the grain interiors (*Meers & Brown*, 1941; *Polushkin*, 1964). This stored energy can be a moving force for a corrosion process.

Another fact which must be taken into consideration is that lower fusing types of gold solder alloys often contain eutectic phases (*Skinner & Phillips*, 1968). Hence because of the resulting lack of surface homogeneity electrolytic couples can occur.

Cold working of the material can induce stress regions thereby creating high energy areas susceptible to corrosion. The tensile stresses can be applied stresses or residual stresses from previous plastic deformation. Because of electrolytic action microcracks can be formed in anodic areas on the material surface. If the applied stress is cyclic in nature it can serve to pump fresh electrolyte into these cracks thus amplifying the process. In the oral cavity a restoration such as for example a soldered bridge can be exposed to cyclic stress during mastication and bruxism.

Compositional heterogeneity of dental gold constructions is very common (*Björn & Hedegård*, 1965; *Söremark et al.*, 1966; *Eick & Hegdahl*, 1968; *Bergman & Björnham*, 1972). In addition foreign inclusions frequently occur. These factors all contribute to the total electrochemical behavior of the dental gold alloys.

Thus the relationship between the content of a single alloy element and its dissolution rate must be viewed bearing in mind the previously discussed metallurgical variables. Morphology and composition at microscopic level determine to a great extent the electrochemical behavior of these alloys.

During the course of the corrosion experiments in the present study a well-defined gas phase consisting of an oxygen-nitrogen mixture was bubbled through the electrolyte solutions. Under clinical conditions differences in oxygen tension between parts of the same restoration do occur. In regions where plaque deposits exist low oxygen concentration areas are found. In spite of this fact these areas will tend to corrode rather than areas of high oxygen concentration (*Greener et al.*, 1972). From this point of view the fairly low oxygen concentration during the experiments in the present study is an advantage as it imitates oral conditions. The accumulation of plaque also furthers variations in the composition of the given electrolyte within the system as the pH value of dental plaque in general rapidly

falls for a short time when sugar is supplied.

In addition it has been shown *in vivo* (*Koivumaa & Mäkilä*, 1970) that galvanic effect (type III casting dental gold alloy versus amalgam) influenced plaque accumulation which was more noticeable in the vicinity of the galvanic test cell than at a distance from it. As galvanism may also affect the metabolic characteristics of micro-organisms the quality of dental plaque may be changed. These examples show how easily the ecology of the system may change within the oral cavity thus making the corrosion behavior of metallic restorations *in vivo* hard to interpret, predict and control.

The present *in vitro* corrosion experiments were performed under circumstances which may be said to represent very unfavourable conditions within the oral cavity. It has been shown that the alloy elements Cd, Cu and Zn under these given circumstances are dissolved from the dental gold solder alloys studied and that the dissolution rate of each of the three elements could be determined.

The cadmium dissolution will now be discussed. As formerly stated a value of $LDR = -6$ corresponds to a dissolution rate of 3.5 mg Cd year $^{-1}$ mm^{-2}. A value of $LDR = -11$ which lies some powers of ten lower in a region where the value of E is about 550—600 mV, see Fig. 4 and Table II, corresponds to a dissolution rate of about 0.04 μg Cd year $^{-1}$ mm^{-2}. The extrapolation is doubtful, however, the value of LDR could not possibly exceed -8. Thus a tentative value of $LDR = -8$ might be of interest. The corresponding dissolution rate is 0.04 mg Cd year $^{-1}$ mm^{-2}. A patient who has a large dental bridge construction with several soldered joints can have an exposed solder area of about 0.5 cm^2. According to the calculations above a dissolution of 2 mg Cd year^{-1} may occur in the oral cavity of this patient.

According to the World Health Organization (WHO) and the Swedish National Board of Health and Welfare the Cd-content of drinking water must not exceed 0.005 mg Cd l^{-1}. Assuming a daily intake of 1 litre of drinking water this corresponds to 1.8 mg Cd year^{-1}.

Taking into consideration different sources of cadmium intake (main source: food) the WHO (1972) has proposed a provisional tolerable weekly intake of 400—500 μg Cd per individual (21—26 mg Cd year^{-1}). In comparison to this the contribution of Cd in man resulting from Cd dissolution from dental gold solders in the oral cavity must be judged to be rather small. However, the biological significance in the long run is hard to estimate at the present time.

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