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A comparative study of the electrochemical corrosion behaviour of dental amalgams

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The electrochemical corrosion behaviour of sixteen currently marketed amalgams for dental fillings was studied *in vitro* under experimental conditions closely resembling those of clinical application. Depending upon the type of amalgam and the treatment of the filling the electrochemical corrosion currents varied over several orders of magnitude; their change as a function of time was also very different. Suggestions are made for a stability rating of the products based on the results obtained.

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1. Introduction

Despite considerable uncertainties with respect to the biological effects of amalgam fillings currently used in dental medicine and a lively discussion of their use and risks [1–5] these materials remain the most popular ones for dental restoration. In West Germany alone, in 1989, 37.8 million amalgam fillings were prepared.

Although the use of heavy, non-noble metals, including mercury and several other metals of high biological toxity as constituents of dental fillings is not desirable, the lack of alternative materials and the long successful use of amalgams maintains their popularity. Because of the known biological effects and the incompatibility of various constituents in amalgams [6] a study of their corrosion behaviour, in particular, a comparative approach of various products is necessary. This need is further enhanced by the fact that the recently expanded application of metal alloys with reduced noble metal content as inlays and crowns leads to a very mixed electrochemical corrosion environment in the oral cavity (for example see [7]). The situation is even more complicated by the growing number of new chemical substances present in foodstuffs and drugs, which may interact with metals in the mouth.

Detailed studies of the composition of solid amalgams containing a variety of metals (Table 1) have revealed several metallic binary and ternary phases of very different susceptibility to corrosion. In particular the phase Sn_8Hg (gamma-2 phase) is prone to corrosion. Subsequent development of non-gamma-2-phase amalgams has led to high copper dispersant alloys (HCD) and high copper single composition alloys (HCSC) [8].

Various techniques have been employed to obtain comparable data on the stability of amalgam filling materials, in particular with respect to their corrosion behaviour (for brief reviews see [5, 9]). Most studies were performed *ex situ* (*in vitro*). Cyclic voltammetry (CV) with an electrolyte solution as close as possible to natural saliva proved to be particularly helpful and easy to perform [9–12]. Unfortunately the experimental results and, thus, the comparability of the various studies depend strongly on the experimental conditions, in particular the composition of the electrolyte solution [9, 13], the scan rate and the sample pretreatment. Further experimental methods, including cyclic voltammetry with widely varying scan rates, used in studies of the corrosion behaviour of metal alloys of low noble metal content have been reviewed elsewhere [14].

Low scan rate CV has been shown to be a method giving results strongly correlated with those of other, in particular *in vivo*, studies of corrosion behaviour [15]. The importance of results from electrochemical corrosion studies is further enhanced by the experimental observation that, after an initial period of about 30 days, the primary corrosion process leading to changes and deterioration of amalgam fillings is electrochemical corrosion [16]. Other experimental methods such as simple rest potential measurements are less informative [2, 12, 17, 18].

In the present study we have used a solution of various salts as suggested by Meyer [19] as synthetic saliva. A very similar solution has been described first by Swartz *et al.* [20]. After modifications applied later by Fusayama *et al.* [21] this solution has been named Fusayama saliva. Its properties are close to those of natural saliva; Ringer's solution, frequently used in corrosion studies, shows an artificially enhanced chloride corrosion [22]. Nevertheless the corrosion products formed in Ringer's solution and *in vivo* are very similar [23]. Differences in results and further arguments in favour of Fusayama saliva are reviewed in [24]. The scan rate of $1\,mV\,s^{-1}$ ($= 60\,mV\,min^{-1}$) was chosen here as a compromise between the ideal of very small scan rates ($\leqslant 1\,mV\,s^{-1}$) and fast scan rates

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Table 1. Composition of selected amalgams(a)

Name & manufacturer	*Ag*	*Sn*	*Cu*	*Zn*	*Alloy/Hg ratio*	*Classification*
1 Caulk Dentsply Valiant-Ph.D.-XT(b)	52%	29.3%	17.5%	–	1.32	HCSC
2 Coltene Oralloy	59%	28%	13%	–	1.01	HCD
3 Degussa Duralloy	50%	30%	20%	–	1.11	HCSC
4 Degussa Standalloy F	71%	25.7%	3.3%	–	n.a.	conventional
5 Heraeus Heragam 48(g)	48%	30%	21.98%	–	1.33	HCSC
6 Johnson & Johnson Dispersalloy(c)	69.5%	17.7%	11.8%	1%	1	HCD
7 Kerr Contour(c,d)	41%	31%	28%	–	n.a.	HCSC
8 Kerr Sybralloy(f)	41%	31%	28%	–	n.a.	HCSC
9 Kerr Tytin	60%	26%	14%	–	n.a.	HCD
10 Merz SiAmKap	69.4%	19.3%	10.9%	0.4%	0.95	HCD
11 Nordiska Epoque 2000 (man. triturated, slight excess of mercury)	43%	29%	25%	0.1%	≈ 1	HCSC
12 Nordiska Epoque 2000 (mechan. triturated)	43%	29%	25%	0.1%	1	HCSC
13 SDI Permite C(c,e)	56%	27.9%	15.4%	0.2%	0.91	HCSC
14 Vivadent Amalcap S.A.S	70.1%	18%	11.9%	–	1.11	HCD
15 Vivadent Vivalloy HR	46.5%	30%	23.5%	–	0.9	HCSC
16 Vivadent Amalcap Plus	70.1%	18%	11.9%	–	0.9	HCD

(a) Compositions as stated by the manufacturer
(b) Palladium enriched (0.3%)
(c) Regular setting type
(d) Particle size $\leqslant 44\,\mu m$
(e) Contains 0.5% Indium
(f) Particle size $\leqslant 5\,\mu m$
(g) Contains 0.02% zirconium
n.a.: predosed in capsules, no ratio declared by manufacturer.

($\geqslant 10\,\mathrm{mV\,s^{-1}}$). A low scan rate is desirable in order to detect even very slow electrochemical processes which might be overlooked when using faster scan rates (for a critical discussion see [7]). Faster scan rates reduce the time for an experiment and avoid irreversible changes of the sample (in particular extensive metal dissolution and passivation) making cyclic voltammetry impossible or at least irreproducible. Steady state measurements give results difficult to reproduce because of the changes taking place at the electrode surface, in particular in the electrode potential range where severe corrosion occurs.

2. Experimental details

Samples of amalgam fillings were triturated and condensed according to manufacturers' instructions into hollow Plexiglas cylinders (for a list of samples and compositions see Table 1). A surface area of $1\,\mathrm{cm}^2$ of amalgam filling was exposed to the electrolyte solution. Before electrochemical measurements the samples were cleaned ultrasonically in ultrapure $18\,\mathrm{M\Omega}$ water; subsequently they were connected to a sample holder fitted with a tapered joint. A conventional electrochemical H-cell with a corresponding tapered joint and cell compartments for a platinum sheet counterelectrode and a saturated calomel electrode acting as a reference electrode separated from the main compartment by glass frits was used.

A modified synthetic saliva containing 0.4 g KCl, 0.4 g NaCl, 0.69 g $NaH_2PO_4 \cdot H_2O$, 0.005 g $Na_2S \cdot 9H_2O$, 0.795 g $CaCl_2 \cdot H_2O$ and 1 g urea per dm^3 dissolved in $18\,\mathrm{M\Omega}$ water (Seralpur pro 90c) was used as electrolyte solution; its pH was 5.00. The solution was saturated with pressurized air filtered with activated carbon. The cell was immersed in a water bath kept at 37 °C. Pressurized air was used instead of nitrogen or argon in order to keep the composition of the electrolyte solution as close as possible to the *in vivo* situation. The results of preceding experiments indicated that any contribution from oxygen reduction in the potential range was negligible.

A potentiostat PCA LB 75 (Bank) was used. The triangular voltage sweep was supplied via a DA-converter from a computer MAC 80 (Spectradata, Oldenburg). The corresponding cell current signal was digitised and stored for further data treatment. A scan rate of $1\,\mathrm{mV\,s^{-1}}$ was applied. The upper potential limit was set to a value low enough to exclude unwanted extensive material dissolution. This value is within the range of electrochemical potentials usually encountered in the mouth. Additional details of the experimental setup and procedure are described elsewhere [25].

In order to simulate the influence of temperature changes on the corrosion behaviour a separate set of samples was exposed alternatively to ice water and water at 60 °C for 5 min each for a total time of one hour (samples thus treated are designated 'tempered'). The effect of polishing the filling was studied after grinding and polishing the samples with abrasive paper (grit 600, 800 and 1000), followed by wet polishing with an Al_2O_3 slurry of 13 and subsequently $3\,\mu m$ particle size (Bikorit, Feldmühle) on a rotating felt disc.

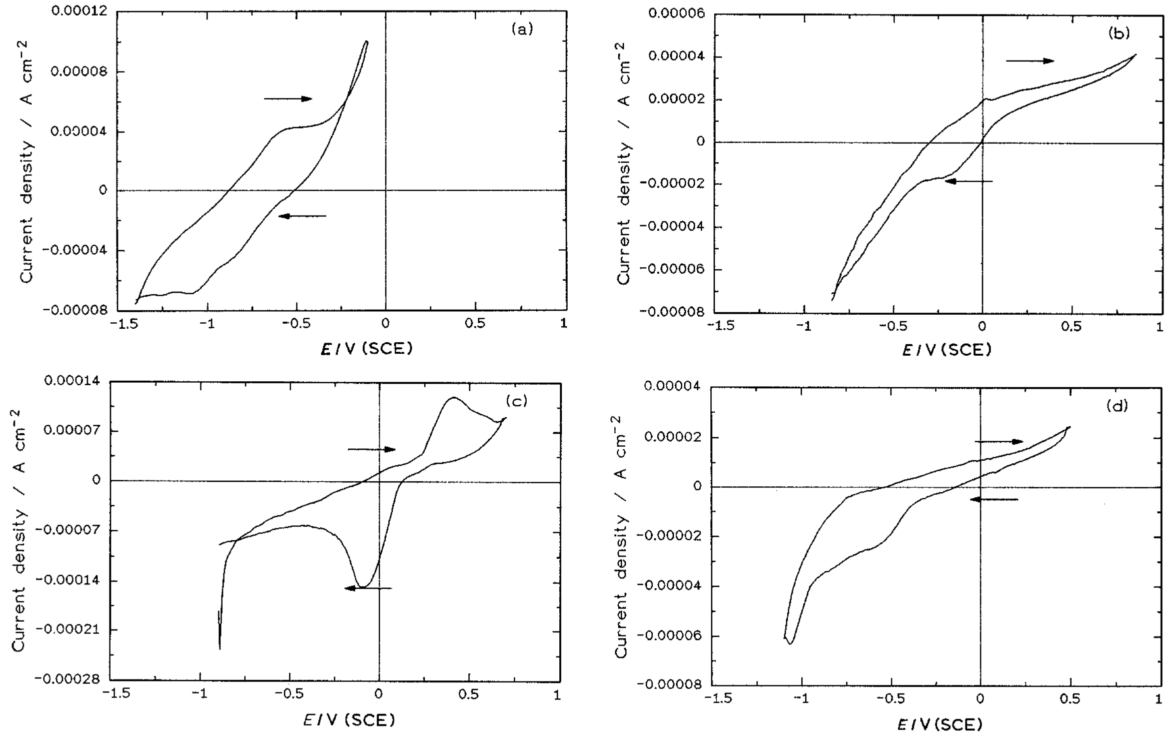

Fig. 1. Cyclic voltamograms of representative amalgam samples: (a) Degussa Standalloy F, (b) Nordiska Epoque 2000 (mechanically triturated), (c) Vivadent Amalcap$^{\mathrm{plus}}$, and (d) Vivadent Vivalloy HR. Scan rate 1 mV s^{-1}, synthetic saliva solution, 37 °C, air saturated.

3. Results

From the CVs, which were in most cases rather featureless (for a typical set of CVs obtained with tempered and polished samples see Fig. 1), no characteristic electrode potentials indicating the onset of corrosion (breakthrough potentials) could be obtained. This behaviour is most likely caused by the mixed composition of the metal amalgam electrode. Essentially composed of several metals these components are present in a number of different binary and ternary phases. Their corrosion behaviour in terms of rate of corrosion, onset of anodic corrosion current, as well as most likely corrosion product, is extremely variable. This also accounts for the different developments of the CV as a function of cycle number (see below).

For a comparison the anodic current density in the tenth CV at an electrode potential which corresponds to an average electrochemical potential of a metal electrode in the saliva within the mouth, is plotted for polished and tempered and polished samples in Fig. 2. The tenth cycle was selected because during the first several cycles changes in the CV shape and the observed currents were observed, whereas in the tenth cycle a steady state behaviour was observed. The selected electrode potential was $E_{\mathrm{SCE}} = 300\,\mathrm{mV}$, this value is positive to the spontaneously established rest potential of the amalgam in contact with the electrolyte solution and within a potential region, where metal dissolution proceeds at a moderate rate allowing comparison of different samples. The value is well below the maximum values measured with gold alloys against amalgams of 700–800 mV [1], the respective potentials against SCE are $E_{\mathrm{Au}} = -200$ to 50 mV and $E_{\mathrm{amalg.}} = -650$ to -100 mV [3]. Lower potential differences between gold and amalgam of 500 mV have been reported earlier [26, 27]. In the case of a few samples, in particular of Standalloy F, the CV could not be recorded up to this value because of vigorous corrosion, in this case the current density at $E_{\mathrm{SCE}} = -100\,\mathrm{mV}$ was determined.

An evaluation of the electrode potentials established spontaneously after immersion of the electrode into the saliva electrolyte solution did not show any correlation with the results obtained from the CVs. At

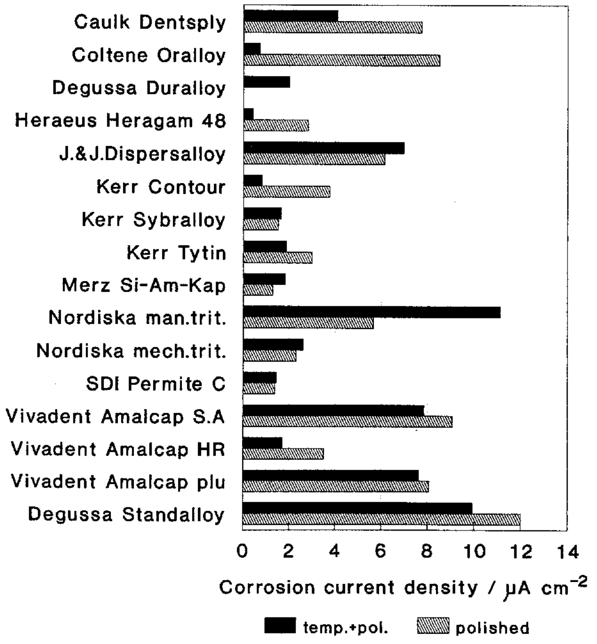

Fig. 2. Plot of corrosion current density at $E_{\mathrm{SCE}} = +300\,\mathrm{mV}$ (Degussa Standalloy F: $E_{\mathrm{SCE}} = -100\,\mathrm{mV}$) for polished and tempered and polished samples.

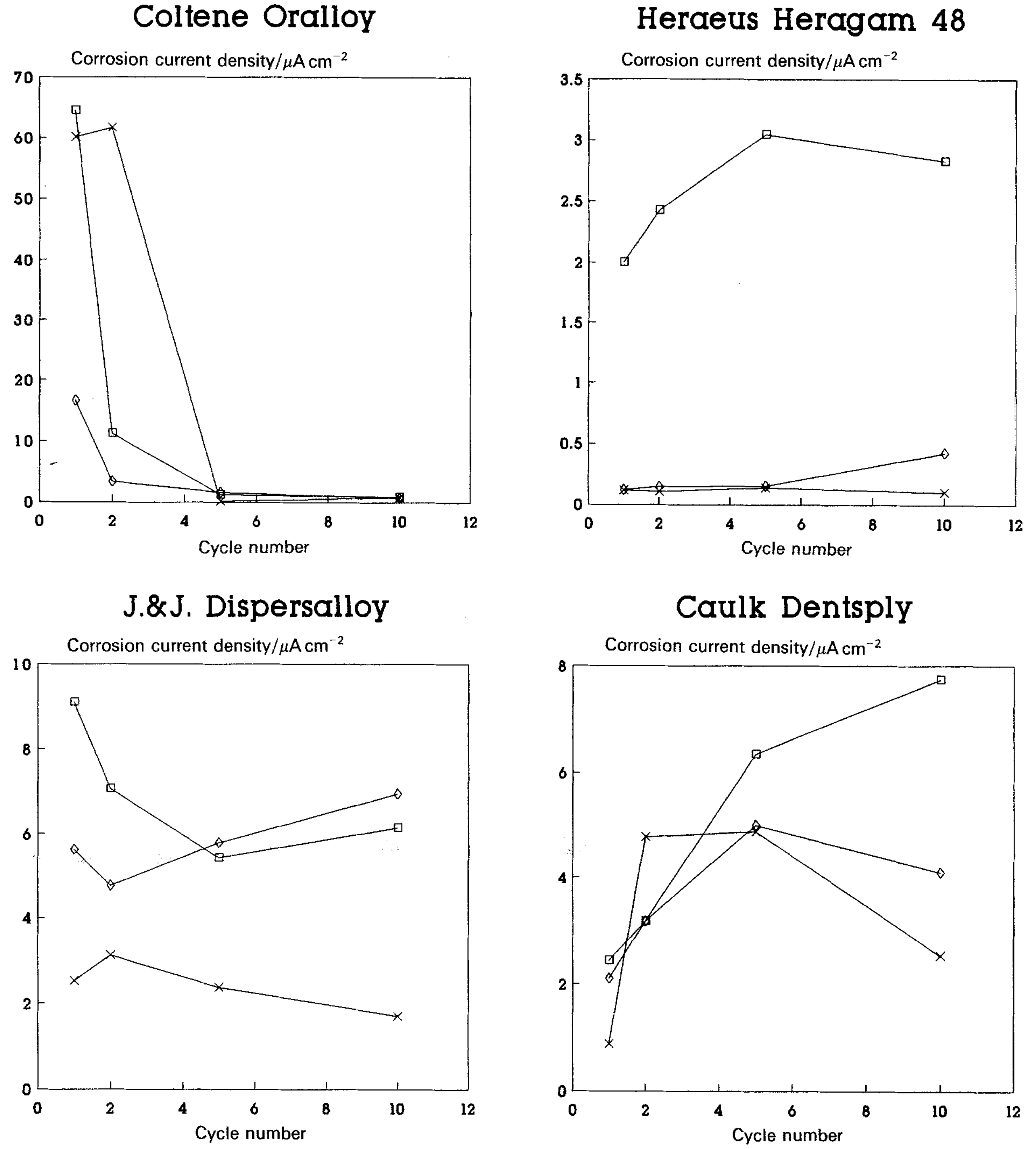

Fig. 3. Plots of corrosion current density as a function of cycle number for selected samples, measurement conditions see Fig. 1, lines serve only as a guide for the eye. (□) Polished, (×) tempered and (◇) tempered and polished.

least in this investigation this very simple electrochemical technique is not useful.

In order to gain further insight into the development of the corrosion behaviour as a function of cycle number (i.e. growing corrosion product layer thickness etc.) these corrosion currents were plotted as a function of cycle number for samples pretreated as discussed (as prepared, prepared and polished, as prepared and tempered, as prepared, tempered and polished). These plots show a distinct development of the corrosion current (compare Fig. 3 for representative set of samples). These observations are considered in further rating of the alloys.

A comparison of all samples after polishing shows a broad variation of observed currents (Fig. 2) with Degussa Standalloy F no values were measured at $E_{SCE} = 300$ mV (see above). In the case of Nordiska Epoque 2000 the difference between the mechanically mixed and the hand mixed samples are significant. This is even more pronounced in a comparison of the corresponding values obtained with tempered and polished samples in Fig. 2. This effect might be caused by an insufficient homogenisation of the alloy–mercury mixture and a subsequently inhibited efficiency of the Cu_3Sn-phase as a getter of superficial tin during solidification. In the case of Kerr Contour and Kerr Sybralloy the only difference between the products is the different particle size of the alloy. The former has an average particle size of $\leqslant 40\,\mu$m, the latter of $\leqslant 5\,\mu$m. The amalgams prepared from these

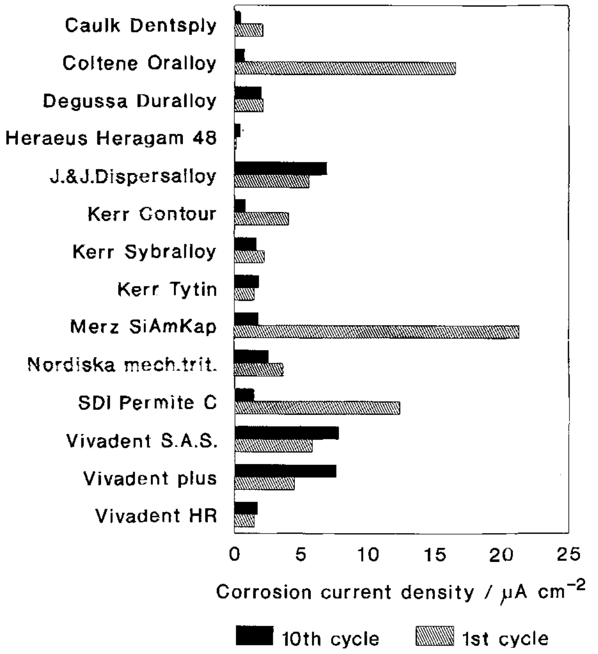

Fig. 4. Plot of corrosion current density at E_{SCE} = +300 mV for tempered and polished samples in first and tenth cycle.

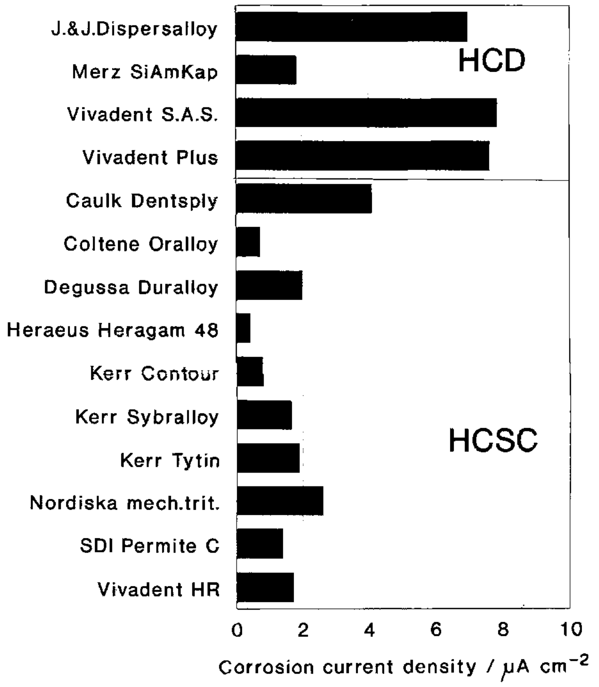

Fig. 5. Plot of corrosion current density at E_{SCE} = +300 mV for tempered and polished samples, grouped according to alloy type.

alloys show a higher corrosion current for the polished samples of the former product, after tempering the latter is the more stable one (*cf.* Fig. 3). Obviously the smaller particle size results in a faster surface coverage with protective corrosion products in the case of the finer particle alloy. Since, during tempering, solid state diffusion and phase changes are accelerated, this advantage disappears, whereas the alloy made with greater particles shows the greater overall longterm stability.

In the case of the remaining samples, some show a further decrease in corrosion current density after tempering, whereas some samples corrode slightly faster. A comparison of the anodic current observed in the first and in the tenth cycle as displayed in Fig. 4 gives a more general picture of the time-dependent evolution of surface layers on the amalgam inhibiting further corrosion. Obviously amalgams with a very low anodic activity, even in the initial cycles, are desirable, since in a practical application, upon mechanical removal of parts of the protective layer anodic dissolution comparable to that observed in the initial cycle would recur.

Comparing the samples grouped according to their alloy type in Fig. 5 demonstrates the higher stability of HCSC-alloys. Of all HCD-alloys, based on the evolution of the corrosion density during cycling only, Merz Si-Am-Cap shows a comparable stability although a very high current density during the initial cycles is observed. This implies a lower stability of the amalgam surface without protective passivation layers; since, after mechanical damage of a filling such a situation will arise these samples are inferior in overall stability. Of the HCSC alloys Kerr Contour and Heraeus Heragam 48 are the most stable ; in terms of time dependent corrosion behaviour the latter is the most promising alloy, based on the present results.

References

[1] R. Marxkors, Habilitationsschrift, Universität Münster (1964).
[2] *Idem*, *Dtsch. Zahnärzteblatt* **24** (1970) 53.
[3] *Idem*, *ibid.* **24** (1970) 117.
[4] *Idem*, *ibid.* **24** (1970) 170.
[5] M. J. Gross and J. A. Harrison, *J. Appl. Electrochem.* **19** (1988) 301.
[6] D. Herrmann, *Dtsch. Zahnärztl. Z.* **40** (1985) 261.
[7] H. Weber, *ibid.* **40** (1985) 254.
[8] R. Kropp, *Phillip J. rest. Zahnmed.* (1986) 114.
[9] J. Geis-Gerstörfer and H. Weber, *Dtsch. Zahnärztl. Z.* **42** (1987) 91.
[10] E. P. Lautenschlager, P. Kollmannsperger and K. Eichner, *Dtsch. Zahnärztl. Z.* **40** (1985) 1107.
[11] N. K. Sarkar and E. H. Greener, *J. Oral. Rehab.* **4** (1977) 55.
[12] E. Stender and H. Marx, *Dtsch. Zahnärztl. Z.* **39** (1984) 775.
[13] J.-M. Meyer and J. N. Nally, *J. Dent. Res.* **54** (1975) IADR/CED Abstr. No. 76.
[14] H. Engel, Dissertation, Universität Mainz (1983).
[15] H. Weber, K. H. Sauer and W. Paulssen, *Dtsch. Zahnärztl. Z.* **40** (1985) 838.
[16] D. Brune, *Scand. J. Dent. Res.* **89** (1981) 506.
[17] D. Gerdes, Dissertation, Universität Bonn (1987).
[18] L. Varsányi, L. Sziráki and L. Kiss, 9th European Congress on Corrosion, Utrecht, The Netherlands, October 2–6, 1989, Ext. Abstr. FU-196.
[19] J.-M. Meyer, *Corr. Sci.* **17** (1977) 971.
[20] M. L. Swartz, R. W. Phillips and M. D. E. Tannir, *J. Dent. Res.* **37** (1958) 837.
[21] K. Fusayama, T. Katayori and S. Nomoto, *ibid.* **42** (1963) 1183.
[22] G. F. Finkelstein and E. H. Greener, *J. Oral. Rehab.* **6** (1979) 189.
[23] N. K. Sarkar, G. W. Marshall, J. B. Moser and E. H. Greener, *J. Dent. Res.* **54** (1975) 1031.
[24] H. Engel, Dissertation, Universität Mainz (1983).
[25] B. Westerhoff, Diploma Thesis, Universität Oldenburg (1991).
[26] J. H. Farell, *Brit. Dent. J.* **104** (1958) 128.
[27] B. L. Hyams, *Int. J. Orthodont. and Dent. Child.* **19** (1933) 883.