

Indian Journal of **Dental Research**

Volume 23

Issue 01

January-February 2012

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Official publication of **Indian Society for Dental Research**

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The effect of urea on the corrosion behavior of different dental alloys

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ABSTRACT

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Objective: Intraoral corrosion of dental alloys has biological, functional, and esthetic consequences. Since it is well known that the salivary urea concentrations undergo changes with various diseases, the present study was undertaken to determine the effect of salivary urea concentrations on the corrosion behavior of commonly used dental casting alloys.

Materials and Methods: Three casting alloys were subjected to polarization scans in synthetic saliva with three different urea concentrations.

Results: Cyclic polarization clearly showed that urea levels above 20 mg/100 ml decreased corrosion current densities, increased the corrosion potentials and, at much higher urea levels, the breakdown potentials.

Conclusion: The data indicate that elevated urea levels reduced the corrosion susceptibility of all alloys, possibly through adsorption of organics onto the metal surface. This study indicates that corrosion testing performed in sterile saline or synthetic saliva without organic components could be misleading.

 Received
 : 31-05-10

 Review completed
 : 08-09-10

 Accepted
 : 27-06-10

Key words: Corrosion, dental/craniofacial material, protein adsorption

A variety of metals and alloys are used in dentistry for the fabrication of restorations. Since the intraoral environment is a near-perfect medium for stimulating corrosion, all alloys used in dentistry are required to possess corrosion resistance. Human saliva is composed of a mixture of organic and inorganic ingredients.^[1] Metallic resistance to corrosion in the oral cavity, thus its biocompatibility, plays an important role in the choice of a restorative material.^[1,2] Insufficient corrosion resistance leads to discoloration and deterioration of mechanical properties while the corrosion products can harm the biological system of the host.^[3]

Corrosion of dental alloys has biological, functional as well as esthetic effects and the use of nonprecious alloys in crown and bridge restorations is a much discussed subject, notably

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Access this article online				
Quick Response Code:	Website:			
	www.ijdr.in DOI: 10.4103/0970-9290.99043			

because the release of metallic components and ions from a prosthetic restoration could be harmful to the health status of a patient. The most important alloys in this respect are nickel-containing alloys which are still used widely in dental restorations but are suspected to cause allergic reactions.^[4-6]

Potentiodynamic polarization methods have been used extensively to study the corrosion of dental implant materials in synthetic saliva.^[7] Multiple studies have shown that CrNi dental alloys will corrode in saliva, 0.9% saline solution, and synthetic saliva.^[8-13] Other studies, however, suggest that CrCo and CrNi alloys exhibit good corrosion resistance under the potential and electrolyte conditions appropriate to synthetic saliva.^[14]

Organic molecules present in saliva such as glycoproteins can be important in corrosion and studies indicate that corrosion inhibition involves the adsorption of organics onto the metal surface.^[9,15-17] Salivary levels of urea are higher in patients with diabetes mellitus and in patients undergoing hemodialysis treatment.^[18-22] It has been previously reported that patients with many concomitant diseases exhibited both reduced salivary flow and higher concentrations of biochemical constituents in their saliva.^[20] Johansson^[23] found that children with dental erosion had higher salivary urea concentrations, while thalassemic patients showed lower salivary urea concentrations.^[24] In view of this, it was decided to evaluate the effect of salivary urea levels on the corrosion behavior of three different casting alloys that are most often used for the fabrication of removable partial denture (RPD) frameworks and for crown-and-bridge castings. The aim of this study was to compare the electrochemical behavior of these dental alloys in synthetic saliva containing different concentrations of urea.

MATERIALS AND METHODS

The dental alloys studied here were as follows:

- Co-Cr-Mo alloy (DEGUSSA, Degussa-Hüls AG/ Germany; 63% Co, 28%Cr, 5% Mo, and 4% minor components).
- Ni-Cr-Mo alloy (Suissor FDX 1500/S2[®]; METALOR, Metaux Précieux SA, Metalor/Switzerland; 63.3% Ni, 23.5% Cr, 8.75% Mo, 1.6% Si, <1% Y, and <1% Fe).
- Au-Pt alloy (Degudent U, Degudent GmbH, DENTSPLY Canada Ltd.; 77.3%.

Au, 9.8% Pt, 8.9% Pd, 0.1% Ir, 1.2% Ag, 0.3% Cu, 0.5% Sn, 1.5% In, 0.2% Re, and 0.2% Fe).

Synthetic saliva was prepared using the formula suggested by Shannon,^[25] Table 1, with the solution pH adjusted to 6.5–7 by using a platinum electrode (Cole-Parmer Instrument Company, Vernon Hills, IL, USA). No fluoride was present in the solution to avoid conflicting effects of this corrosive anion.

The urea levels used in this study were based on the findings of Jenkins,^[2] namely 200 mg/l (i.e., average value), 120 mg/l (minimum value) and 700 mg/l (maximum value). The test solutions were prepared using commercially available urea (Sigma[®] chemical company) and weighing was performed on a Mettler AE 100[®] precision balance. The control solution was synthetic saliva without urea. All test media were maintained at 37±1°C (Mariner Heater and Thermostat, Springfield Electrical Co. Ltd., Thruxton Industrial Estate-Nr-Andover; Hampshire SP 11 8PW). Corrosion tests were performed with an EG & G, PAR Model 273 potentiostat and M352 Corrosion Analysis software at scanning rate of 0.5 mV/sec. A standard three-electrode cell consisting of the alloy sample as the working electrode, a saturated calomel reference electrode (SCE) and a graphite counter

Table	1: TI	he	composition	of	synthetic	saliva	solution ²⁵
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Reagent	Addition level (mg) for a total				
g	volume of 2 liters				
NaF	8.4				
NaCl	2560.0				
CaCl2	332.97				
MgCl ₂ .6H ₂ O	250.0				
KCI	89.48				
CH [°] COOK	15.0				
K,PO,.3H,O	772.0				
H _y PO ₁ (85%)	0.1 ml				

electrode was used for the polarization studies. Each metal test specimen was cast as a cylinder (6 mm in height and 16 mm in diameter) and was seated in a Teflon holder with an exposed surface area of 7.5 mm², all other surfaces being coated with sticky wax to prevent crevice corrosion.

Before corrosion testing, all specimens were wet ground successively with 220, 500, 600, 800, and 1200 grit silicon carbide abrasive papers. After polishing, each specimen was ultrasonically cleaned in distilled water followed by ethanol rinsing prior to testing.

Each alloy was tested in the three test media. The control solution, the potentiostat and associated software plotted the polarization curves. General anodic electrochemical behavior, corrosion current densities (μ A/cm²), corrosion potentials (mV), anodic and cathodic Tafel slopes (mV/ decade), and pitting potentials (mV), were recorded and the latter was evaluated by cyclic polarization. All polarization studies were performed in triplicate.

RESULTS

The cyclic polarization curves of CrCo, CrNi, and AuPt in synthetic saliva with the three different urea concentrations are shown in Figures 1–3. The mean values (and their standard deviations) of the test parameters [corrosion potential (E_{corr}), corrosion current density (I_{corr}) and breakdown potentials] for the three test alloys in the plain synthetic saliva solution and with different urea concentrations at 37°C are presented in Table 2.

The polarization behavior of CrCo indicated that the corrosion potential (E_{corr}) shifted in the anodic direction with increase in the solution urea level [Figure 1 and Table 2]. These shifts were statistically significant (P<0.001). There was a dramatic increase in I_{corr} for the 120 mg/l and 200 mg/l solutions (P>0.001) compared to the control but there was a marked drop I_{corr} for the 700 mg/l urea solution (P>0.001) [Table 2]. The breakdown potentials shifted anodically for the CoCr alloy in all media compared to the control (P<0.001) although it was found that there was no difference (P>0.05) in the breakdown potentials ($E_{\rm B}$) for the 200 mg/l and 700 mg/l solutions.

The cyclic polarization curves for CrNi alloy showed little difference in behavior for synthetic saliva alone and with different urea levels [Figure 2]. Further, the hysteresis loop of cyclic polarization curves for the CrNi alloy was far narrower than that observed with the CrCo alloy. While there was an anodic shift in the corrosion potential E_{corr} (*P*<0.001) for this alloy in synthetic saliva with increasing urea concentration, the potential shift (ca. 180 mV) was less than that for CrCo (ca. 330 mV) in the 700 mg/l solution. There was no difference (*P*<0.05) in E_{corr} in the 120 and 200 mg/l solutions. It was found

Table 2: Mean values and standard deviations of *E*_{corr}, *I*_{corr} and brakdown potentials (EB) for CrCo, CrNi and AuPt alloys in synthetic saliva containing different urea

	•			
	Urea level (mg/L)	E _{corr} (mV)	I _{corr} (μΑ /cm ₂)	EB (mV)
CrCo	0	-444.0 ± 3.6	0.52 ± 0.0	454.3 ± 4.0
	120	-279.3 ± 7.0	5.71 ± 0.12	548.3 ± 3.1
	200	-235.3 ± 6.8	5.34 ± 0.05	545.7 ± 2.5
	700	-116.3 ± 4.9	0.84 ± 0.7	611.3 ± 3.5
CrNi	0	-401.0 ± 9.5	1.15 ± 0.01	224.0 ± 4.0
	120	-181.7 ± 3.5	6.45 ± 0.06	631.7 ± 4.0
	200	-185.7 ± 7.0	5.95 ± 0.05	634.0 ± 2.6
	700	-219.3 ± 7.8	0.43 ± 0.04	675.3 ± 3.5
AuPt	0	1066.0 ± 9.8	3.13 ± 0.05	1239.7 ± 4.5
	120	1078.7 ± 3.2	3.20 ± 0.03	1243.7 ± 2.3
	200	1108.3 ± 7.8	2.87 ± 0.02	1264.3 ± 3.8
	700	1154.3 ± 6.0	2.70 ± 0.03	1293.7 ± 4.7



Figure 1: Polarization curves of CrCo alloy in different urea concentrations (12mg-20mg-70mg)



Figure 3: Polarization curves of AuPt alloy in different urea concentrations (12 mg-20 mg-70 mg)

that $I_{\rm corr}$ increased markedly in the 120 mg/L and 200 mg/L solutions compared to the control but there was a marked drop $I_{\rm corr}$ for the 700 mg/l urea solution [Table 2]. Similar to the CrCo alloy, the CrNi alloy showed a marked shift in the breakdown potential with increasing urea concentration but the shift was larger (450 mV) for CrNi than that for CrCo (150 mV).

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Figure 2: Polarization curves of CrNi alloy in different urea concentrations (12mg-20mg-70mg)

The cyclic polarization curves for the AuPt alloy showed few apparent differences between the behavior in the control and test solutions and no significant hysteresis loop was evident in any of the polarization curves [Figure 3]. Small but statistically significant (P<0.01 or P<0.001) anodic shifts in E_{corr} were noted in the 200 and 700 mg/l solutions but there was no difference (P>0.05) in E_{corr} for plain synthetic saliva and saliva containing 120 mg/l. Variation was noted in I_{corr} values in the four test media with significant differences (P<0.001) in the 200 and 700 mg/l solutions but not the 120 mg/l solution (P>0.05). The breakdown potential ($E_{\rm B}$) of the AuPt alloy shifted anodically in the 200 and 700 mg/l solution, (P<0.001) but not in the 120 mg/l solution (P>0.05).

DISCUSSION

A prosthetic restoration releasing metallic ions due to corrosion can be harmful to the health status of a patient and the greatest concern is directed at nickel-containing alloys because of their association with allergic reactions.^[4-6] Any factor that might enhance such metal ion release clearly has clinical significance. The present study is part of an ongoing program of work evaluating the effect of organic salivary components on the corrosion of dental metals in artificial saliva. Traditionally, noble metals were the alloys of choice for the fabrication of prostheses but as precious metal costs rose, the trend has been toward the greater use of base metal alloys, notably chromium-containing alloys, for prostheses. Chromium is added to nickel alloys in order to enhance corrosion resistance through surface oxide film formation. Additions of 16-27% chromium are reported to provide optimal corrosion resistance, while small additions of molybdenum enhance corrosion resistance, specifically to pitting.^[10] Nickel alloys with lower chromium contents do not form a sufficiently protective oxide layer. Similar considerations apply to cobalt-base alloys. Several studies have shown variation in salivary urea levels with different diseases.^[18-23] Since glycoproteins have been shown to be important with regard to corrosion, it is to be expected that changes in salivary urea levels will affect the corrosion behavior of dental alloys.[9,15-17]

The findings of the present study indicate that increasing urea concentrations in a solution affect the electrochemical behavior of the tested nonprecious alloys. In particular, increased levels of urea in synthetic saliva cause a shift of the breakdown potential (E_{p}) in the positive direction. These data suggest that increasing urea levels can decrease both the initiation and the propagation of localized (pitting) corrosion. While the experimental results presented here showed that no hysteresis loop occurred for AuPt and that for CrNi was very small, the hysteresis loops observed for CrCo were much greater, suggestive of pitting susceptibility within the environment with higher urea concentrations. Thus the present findings indicating that AuPt and CrNi alloys should exhibit good resistance to pitting are at variance with other work which showed that CrNiMo alloys are susceptible to crevice attack and to pitting as well as retardation of repassivation under almost all experimental conditions.^[8] Further, the polarization hysteresis loops suggest that CrCo alloy appears to be susceptible to pitting corrosion at all urea concentrations, a finding that appears to be at variance to a previous study.^[9] The latter study reported, on the basis of cyclic polarization tests, that the corrosion resistance of CrCo alloy was improved in synthetic saliva solutions containing different salivary organics. It would appear, therefore, that urea in fact may reduce the resistance of CrCo alloys to pitting attack whereas other salivary proteins have a protective effect.

A surprising finding was that while there was an anodic shift in E_{corr} for all alloys with increasing urea levels in solution, I_{corr} appeared to increase, particularly for CrCo and CrNi in the 120 and 200 mg/L solutions although net decreases were found for CrNi and AuPt in the 700 mg/L solution. Further, the high I_{corr} values for AuPt in all media were unexpected, particularly since SEM studies indicated little if any attack on the metal surface.^[26-28] These results suggest that the observed I_{corr} values may in fact not reflect metal corrosion but rather electrochemical activity of the

urea at the metal surface which results in high current flow but not necessarily metal dissolution.

The findings clearly demonstrate that both the presence and the concentration of urea affected the corrosion behavior of dental alloys. This study indicates that corrosion studies that are performed in synthetic saliva solutions that do not contain salivary proteins may yield misleading results and, particularly, higher corrosion rates than may actually be found in the clinical situation. In particular, since organic components in saliva (notably proteins) can build a pellicle layer which can serve as diffusion barrier for ionic components,^[29] it is possible that a reduced susceptibility to pitting attack may occur over time due to these proteinaceous salivary components. The development of organic layers on the metal surface has been reported to yield unexpectedly low corrosion potentials and to slow the cathodic oxygen reduction reaction, presumably through cathodic polarization.^[30,31] Overall, the present study and the findings of other studies indicate that caution should be exercised in recommending nonprecious alloys for prosthetic restorations. However, the present findings suggest that for patients with systemic diseases that result in increased salivary urea levels or patients with reduced salivary flow rates that result in increased levels of salivary urea, the CrNi alloy could have satisfactory corrosion resistance. In particular, the relatively corrosion resistant behavior of CrNi alloy in synthetic saliva with higher urea concentrations indicates that it would be a reasonable alternative to CrCo alloys for a patient with higher salivary urea levels that cannot afford precious metal alloys. Since results are contradictory to those obtained for tests with salivary proteins,^[9] further studies testing the effect of urea and proteins on corrosion resistant behavior of CrNi alloy are needed to draw precise conclusions. Nevertheless, caution over the use of nickel-based alloys should be exercised for patients with a history of nickel allergy.

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How to cite this article: Geckili O, Bilhan H, Bilgin T, Anthony von Fraunhofer J. The effect of urea on the corrosion behavior of different dental alloys. Indian J Dent Res 2012;23:75-9.

Source of Support: Nil, Conflict of Interest: None declared.