Comparative Evaluation of the Initial Corrosion of four Brands of High Copper Dental Amalgams

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Statement of Problem: Many attempts have been made in order to evaluate the amalgam corrosion behavior as an indicator of biocompatibility.

Purpose: The aim of this study was to evaluate and compare the initial corrosion of four different brands of dental amalgams.

Materials and Methods: Four different types of commercial high copper dental amalgam were studied. A special mold was used and twenty-one samples of each type of commercial dental amalgams were prepared. X-ray diffraction technique was used to investigate the microstructure of freshly prepared specimens. Electrochemical potentiodynamic tests were performed in physiological solutions in order to determine and compare the corrosion behavior of freshly prepared sample of four brands of dental amalgams. The physiological solutions were the Ringer’s solution and physiological normal saline. Five replicate tests on each group of specimens were performed. Tafel extrapolation and linear polarization methods determined corrosion potentials and corrosion current densities. The mean value and standard deviations of the results were calculated. The mean values were statistically compared by ANOVA and Duncan methods at 95% level of confidence.

Results: Gamma-2 phase was present in freshly prepared sample of each type of commercial amalgam. The results showed statistically significant differences between the mean corrosion current density values of freshly prepared sample of four brands of amalgams (P<0.05). The freshly prepared specimen of Sybraloy dental amalgam possesses the higher initial corrosion resistance than the other three, and Cinaalloy dental amalgam possesses the lowest corrosion resistance. This trend is independent to the type of physiological environment.

Conclusion: Initial corrosion resistance of each type of commercial dental amalgam is much less than its corrosion resistance that could be obtained after one week. From the viewpoint of the corrosion behavior as an indication of biocompatibility and for prediction of biocompatibility of the amalgam restoration, it is necessary to pay attention to the initial corrosion of dental amalgam.

Key words: Dental amalgam; Amalgam corrosion; Initial Corrosion; Biocompatibility

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Amalgam restorations are often susceptible to tarnish and corrosion in the oral environment. Dental amalgam galvanically corrodes in mouth. The likelihood of galvanic corrosion increases if two phases are present. Dental amalgams always have more than two
phases, and they also exist in a corrosive environment, like oral cavity. Therefore, amalgams corrode and eventually fail.\(^\text{(2)}\)

The degree of corrosion, tarnish and the resulting discoloration appear to depend on a given individual’s oral environment and, to a certain extent, on the particular alloy employed.\(^\text{(3)}\)

Corrosion of dental amalgam can cause galvanism and galvanic action besides the damaging of restorative metal.\(^\text{(3)}\) The ion release as the result of corrosion is more important and discussion about this matter has been continued.\(^\text{(4)}\) Excessive corrosion can lead to increased porosity, reduced marginal integrity, loss of strength, and the release of metallic products into the oral environment.\(^\text{(5)}\)

In low-copper amalgams, the most corroducible phase is the Tin-Mercury, or gamma-2 (γ₂) phase. Even though a relatively small portion of the amalgam mass consists of the γ₂ phase, in time and in an oral environment the structure of such an amalgam will contain a higher percentage of corroded phases. On the other hand, neither the gamma (γ) nor the gamma-1 (γ₁) phase is corroded easily. Corrosion results in the formation of Tin oxchloride from the Tin in the γ₂ and also liberates Mercury.\(^\text{(5,6)}\) The high Copper amalgams do not have any γ₂ phase in the final set mass. The η phase formed with high Copper alloys has better corrosion resistance.\(^\text{(5,6)}\)

Various types of tests and experimental methods have been used to determine the corrosion behavior of dental amalgams.\(^\text{(7,8)}\)

One of the most important tests for evaluating amalgam corrosion behavior is electrochemical test. Many studies have been performed by this method\(^\text{(6,11)}\) because it has been proved that electrochemical tests are useful, valid and reliable.\(^\text{(12)}\)

The previous works by the authors showed that the powder particle shape of amalgam and the clinical procedures could affect the final surface roughness of the commercial dental amalgams and consequently could affect their corrosion behavior.\(^\text{(13-15)}\) It is noticeable that evaluation of the corrosion behavior had been performed one week after amalgam triturations. Therefore, the results could show the corrosion behavior of high Copper dental amalgams that had no γ₂ phase in their microstructure.\(^\text{(13-15)}\)

The aim of this study was to evaluate and compare the initial corrosion of freshly prepared sample of four brands of dental amalgams.

### Materials and Methods

Four types of commercial amalgam powders with different particle shapes (lathe cut, spherical, spheroidal) were studied. The amalgams used were Sybraloy (Kerr, USA), CinaLux (Shahid Faghihi, Iran), Oralloy (Coltene, USA), and Cinaalloy (Shahid Faghihi, Iran). Chemical composition, particle shapes, and manufacturers of each brand amalgam are given in table 1.

Each type of amalgam alloy was triturated according to the manufacturer’s instructions in a mechanical triturator (Deomat 3, Degussa, Germany) and hand-condensed into special mold by condenser (Φ 3 mm, Aesculap, Germany) by one investigator.

Twenty-one samples of each type of amalgam were prepared at room temperature. For all samples the mold cavity was overfilled and excess amalgam was removed with a new Ward’s carver (Aesculap, Germany), by repeated carving (ten times in the same direction).

One freshly prepared sample of each type of dental amalgam was utilized immediately after preparation for microstructure characterization by X-ray diffraction (XRD) technique.

XRD technique (Philips X’Pert-MPD System with a CuKα wave length of 1.5418 Å) was used to analyse the microstructure and phases present in the four different brands of dental amalgams.

Twenty samples of each type of dental amalgam were utilized for initial corrosion behavior.
evaluation by electrochemical polarization test. Freshly prepared sample of each type of amalgam was washed in the electrolytic solution immediately after preparation and then immersed at 37±1°C for 20 minutes. Electrochemical corrosion polarization test was performed at 37±1°C.

An electrochemical corrosion polarization test cell was used for in vitro potentiodynamic corrosion tests in two different types of physiological solutions. Graphite was used as the counter electrode and saturated calomel electrode (SCE) as a reference electrode.

The physiological solutions were the Ringer’s solution (0.86 wt% NaCl, 0.03 wt% KCl, and 0.033 wt% CaCl₂) and physiological normal saline (0.9 wt% NaCl).

Dynamic polarization curves were recorded at a potential scanning rate of 0.5mV S⁻¹ initiated at 250 mV blow the open circuit potential and the atmosphere was open to air. Ten replicate tests of each group of specimens were performed.

To compare the initial corrosion behavior of four brands of dental amalgams, samples were dynamically polarized in two different types of physiological solutions. Potentiodynamic polarization curves were determined at 37±1°C using an EG&G model 263A potentiostat/galvanostat interfaced with a computer and a recorder.

The anodic and cathodic polarization curves have been obtained for each sample and corrosion potentials and corrosion current densities were determined by Tafel extrapolation and linear polarization methods. The mean value and standard deviations of the results were calculated. Data were analyzed using one-way ANOVA and Duncan post HOC test.

Results
The X-ray diffraction patterns of freshly prepared specimen of four brands of dental amalgams are shown in figures 1, 2, 3, and 4. The peaks of γ, γ₁, and γ₂ phases could be identified in all XRD patterns. Results indicate that the γ₂ phase was present in freshly prepared sample of each type of commercial dental amalgam.

The potentiodynamic polarization curve of freshly prepared sample of the Sybraloy amalgam in the normal saline solution is shown in figure 5. Similar curves of the CinaLux, Oralloy, and Cinaalloy obtained in normal saline solution are plotted in figure 5 too.

These curves were selected because their extracted data were the most nearest to the mean values of the current densities of each group of specimens. The results showed statistically significant differences between the mean corrosion current density values of freshly prepared specimens of four different types of the commercial dental amalgams (P<0.05).

The Sybraloy dental amalgam possessed the lower corrosion current density than the others. The Cinaalloy dental amalgam possessed the highest corrosion current density and thus the lowest corrosion resistance.

The mean values of corrosion current density and corrosion potential of each type of dental amalgams in normal saline solution are summarized in table II. Corrosion current densities as determined by the linear polarization method are also given in table II.

The similar potentiodynamic polarization curves that are obtained in Ringer’s solution are plotted in figure 6.

The results showed statically significant differences between the mean corrosion current density values of freshly prepared specimens of four different types of the commercial dental amalgams (P<0.05).

The similar trend can be observed in the Ringer’s solution. The mean values of corrosion current density and corrosion potential of each type of dental amalgams in Ringer’s solution are summarized in table III. Corrosion current densities as determined by the linear polarization method are also given in table III.
Fig. 1- X-ray diffraction (XRD) pattern of freshly prepared specimen of the Sybraloy dental amalgam.

Fig. 2- X-ray diffraction (XRD) pattern of freshly prepared specimen of the Cinalux dental amalgam.
Fig. 3- X-ray diffraction (XRD) pattern of freshly prepared specimen of the Oralloy dental amalgam

Fig. 4- X-ray diffraction (XRD) pattern of freshly prepared specimen of the Cinalloy dental amalgam
Fig. 5- Potentiodynamic polarization curves of four different types of commercial high copper dental amalgams in the normal saline solution at 37°C

Fig. 6- Potentiodynamic polarization curves of four different types of commercial high copper dental amalgams in the normal Ringer’s solution at 37°C

Table I- Chemical composition, powder particle shapes, and the manufacturer of four types of commercial amalgams

<table>
<thead>
<tr>
<th>Commercial Amalgam</th>
<th>Chemical Composition (%)</th>
<th>Particle Shape</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sybraloy</td>
<td>40 Ag, 30 Sn, 30 Cu</td>
<td>Spherical</td>
<td>Kerr (USA)</td>
</tr>
<tr>
<td>CinaLux</td>
<td>45 Ag, 30 Sn, 25 Cu</td>
<td>Spherical</td>
<td>Faghidi (Iran)</td>
</tr>
<tr>
<td>Oralloy</td>
<td>59 Ag, 28 Sn, 13 Cu</td>
<td>Spheroid</td>
<td>Colhene (USA)</td>
</tr>
<tr>
<td>Cinalloy</td>
<td>45 Ag, 30 Sn, 25 Cu</td>
<td>Lathe-cut</td>
<td>Faghidi (Iran)</td>
</tr>
</tbody>
</table>

Table II- Mean values ± standard deviation of initial corrosion current densities and corrosion potentials of four types of commercial dental amalgams in normal saline solution at 37°C

<table>
<thead>
<tr>
<th>Commercial Amalgam</th>
<th>Procedure</th>
<th>$I_{corr}$ (mA)</th>
<th>$E_{corr}$ (mV)</th>
<th>$I_{corr}$ (nA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sybraloy</td>
<td>Carving</td>
<td>$-5212$±25</td>
<td>$9185$±581</td>
<td>$8816$±612</td>
</tr>
<tr>
<td>CinaLux</td>
<td>Carving</td>
<td>$-5562$±28</td>
<td>$16233$±1391</td>
<td>$13942$±1106</td>
</tr>
<tr>
<td>Oralloy</td>
<td>Carving</td>
<td>$-5392$±26</td>
<td>$25171$±1992</td>
<td>$18942$±1385</td>
</tr>
<tr>
<td>Cinalloy</td>
<td>Carving</td>
<td>$-4112$±31</td>
<td>$32120$±2671</td>
<td>$22125$±2112</td>
</tr>
</tbody>
</table>

Table III- Mean values ± standard deviation of initial corrosion current densities and corrosion potentials of four types of commercial dental amalgams in Ringer’s solution at 37 °C

<table>
<thead>
<tr>
<th>Commercial Amalgam</th>
<th>Procedure</th>
<th>$I_{corr}$ (mA)</th>
<th>$E_{corr}$ (mV)</th>
<th>$I_{corr}$ (nA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sybraloy</td>
<td>Carving</td>
<td>$-5164$±19</td>
<td>$8061$±392</td>
<td>$6893$±285</td>
</tr>
<tr>
<td>CinaLux</td>
<td>Carving</td>
<td>$-5554$±17</td>
<td>$10175$±812</td>
<td>$9095$±511</td>
</tr>
<tr>
<td>Oralloy</td>
<td>Carving</td>
<td>$-5354$±21</td>
<td>$13144$±1007</td>
<td>$11852$±835</td>
</tr>
<tr>
<td>Cinalloy</td>
<td>Carving</td>
<td>$-4714$±16</td>
<td>$19720$±1581</td>
<td>$15895$±1022</td>
</tr>
</tbody>
</table>
Discussion
Although dental amalgam has been used for more than 150 years, it is now being questioned more or less vigorously as a dental restoration material due to its alleged health hazard, corrosion products, biological toxicity and environmental hazards. Concerns have been expressed about the toxicity of dental amalgam, in particular with respect to marginal fracture, surface degradation, corrosion, and release of corrosion products and biocompatibility.\(^{(15)}\) Study and research about the corrosion and tarnish of dental amalgam have been continued during recent decades and still are ongoing.\(^{(3,5,15)}\)

Corrosion behavior is an indicator of biocompatibility of dental materials, especially in the case of dental amalgam.\(^{(13)}\) Corrosion currents between precious dental materials and dental amalgam restorations were one of the first raised concerns. Also electrode potential between different types of amalgams, and between dental amalgam restorations and other metallic constructions, have been observed.\(^{(16)}\) It has been reported that the presence of amalgam fillings do not appear to affect the general health of patients, and it can be stated that epidemiological studies of amalgam bearers have not as yet detected increased incidence of cancer, cardiovascular disease, diabetes, early death and subjectively reported ailments.\(^{(17)}\) Although, some researchers have even suggested that the use of amalgams should be discontinued.\(^{(18)}\) Others conclude that amalgam restoration remain safe and effective.\(^{(19)}\) According to figures 1, 2, 3, and 4, the \(\gamma_2\) phase was present in freshly prepared specimens of all commercial dental amalgam during two hours after amalgam triturating. This means that high copper dental amalgam is more susceptible to corrosion and the situation is more conductive to the formation of corrosion products during the initial two hours after triturating.

According to table II and figure 5, the freshly prepared specimen of Sybraloy amalgam possessed lower corrosion current density \([E_{\text{corr}}=531\pm25 \text{ mV}, i_{\text{corr}}=9185\pm581 \text{ nA/cm}^2]\) than the others. The Cinaalloy dental amalgam possessed the highest corrosion current density and thus the lowest corrosion resistance \([E_{\text{corr}}=-411\pm31 \text{ mV}, i_{\text{corr}}=52120\pm2671 \text{ nA/cm}^2]\). The similar trend could be observed in the Ringer’s solution (Fig. 6, Table III). This result is in agreement with the previous findings of the present authors.\(^{(15)}\) The magnitudes of the initial corrosion current densities (Table II) are much more than the specimens that had been evaluated one week after amalgam triturating and samples preparation.

The high copper amalgams do not have any \(\gamma_2\) phase in the final set mass. This phase would be eliminated during 24 hours after amalgam triturating.\(^{(3)}\) Since the \(\gamma_2\) phase is the most anodic phases of the present phases in set amalgam alloys, the high copper amalgams that virtually eliminate this phase, show improved laboratory corrosion behavior compared with traditional amalgams.\(^{(4)}\)

In the present research, the corrosion polarization tests were performed immediately after dental amalgam trituration. As the results indicate (Figs 1-4), the tests were performed when the \(\gamma_2\) phase wasn’t eliminated in amalgam microstructure.

The results indicate that initial corrosion resistance of each type of commercial high copper dental amalgam is much less than its corrosion resistance that could be obtained after one week. The ranking of initial corrosion resistance of four types of commercial amalgams is similar to their corrosion resistance after one week. It means that the ranking of corrosion behavior has been stable but the results show that the magnitudes of corrosion have been changed severely.

Conclusion
Initial corrosion resistance of each type of commercial dental amalgam is much less than its corrosion resistance that could be obtained
after one week. From the viewpoint of the corrosion behavior as an indication of biocompatibility and for prediction of biocompatibility of the amalgam restoration, it is necessary to pay attention to the initial corrosion of dental amalgam.

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References: