

## Review Article

### A Review on Dental Amalgam Corrosion and Its Consequences

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#### ABSTRACT

Dental amalgam is still the most useful restorative material for posterior teeth and has been successfully used for over a century. Dental amalgam has been widely used as a direct filling material due to its favorable mechanical properties as well as low cost and easy placement. However, the mercury it contains raises concerns about its biological toxicity and environmental hazard. Although in use for more than 150 years, dental amalgam has always been suspected more or less vigorously due to its alleged health hazard.

Amalgam restorations often tarnish and corrode in oral environment. Corrosion of dental amalgam can cause galvanic action. Ion release as a result of corrosion is most important. Humans are exposed to mercury and other main dental metals via vapor or corrosion products in swallowed saliva and also direct absorption into blood from oral mucosa. During recent decades the use of dental amalgam has been discussed with respect to potential toxic effects of mercury components.

In this article, the mechanisms of dental amalgam corrosion are described and results of researches are reviewed. It finally covers the corrosion of amalgams since this is the means by which metals, including mercury, can be released within oral cavity.

**Keywords:** Dental amalgam, Amalgam corrosion, Biocompatibility, Mercury release, Amalgam restoration

One of the primary conditions of any metal used in the mouth is that it must not produce corrosion products that will be harmful to the body<sup>1</sup>. Corrosion is a chemical or electrochemical process through which a metal is attacked by natural agents, resulting in partial or complete dissolution, deterioration, or weakening of any solid substance<sup>2</sup>.

Oral environment is very susceptible to corrosion products formation. Mouth is always moist and is continually subjected to fluctuations in temperature. Food and liquids ingested have wide ranges of pH. Acids are released during the breakdown of foodstuffs. All of these environmental factors contribute to the degrading process known as corrosion<sup>2</sup>.

Tarnish is a surface discoloration on a piece of metal. In oral cavity, tarnish often occurs from the formation of hard and soft

deposits on the surface of the restoration. The soft deposits are plaques and films composed mainly of microorganisms and mucin. Surface discoloration may also arise on a metal from the formation of thin films, such as oxides, or sulfides. Tarnish is an early indication of corrosion<sup>1</sup>.

Corrosion in the specific sense is not merely a surface deposit but is an actual deterioration of a metal by reaction with its environment. It causes severe and catastrophic disintegration of the metal body. This disintegration of the metal may occur through the act of moisture, atmosphere, acids, alkalies or certain chemicals.

Various sulfides, such as hydrogen or ammonium sulfide, corrode silver, mercury, and similar metals present in amalgam<sup>2, 3</sup>. Water, oxygen, and chloride ions are present in saliva and contribute to corrosion attack.

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Various acids such as phosphoric, acetic, and lactic are present at times. At the proper concentration and pH, these can lead to corrosion<sup>3</sup>. Specific ions may play a major role in the corrosion of certain alloys. For example, oxygen and chlorine are implicated in corrosion of amalgam at the tooth interface and within the body of the alloy<sup>3,4</sup>.

Composition, physical state, and surface condition of a metal, as well as the chemical components of its surrounding medium determine the nature of corrosion reactions. Other important variables affecting corrosion processes are temperature, temperature fluctuation, movement or circulation of the medium in contact with the metal surface, and the nature and solubility of corrosion products<sup>2</sup>. Many types of electrolytic corrosion are possible and all may occur to some extent in oral cavity because saliva, with the salts it contains, is a weak electrolyte. The electrochemical properties of saliva depend upon its composition, concentration of its components, pH, surface tension, and buffering capacity<sup>1</sup>.

The types of electrolytic corrosion are based upon the mechanisms that produce the inhomogeneous areas (anodic and cathodic areas) and thus the net result would be an electric couple action<sup>1,3</sup>. An important type of electrolytic corrosion occurs when combinations of dissimilar metals are present in oral cavity and is known as galvanic corrosion or dissimilar metals. Another type of galvanic corrosion is due to the heterogeneous composition of the metal surface. Example of this type may be the eutectic and peritectic alloys. The other type of electrolytic corrosion is called concentration cell corrosion or crevice corrosion. This situation exists whenever there are variations in the electrolytes or in the composition of the given electrolyte within the system. There are often accumulations of food debris in the interproximal areas of the mouth. This debris then produces one type of electrolyte in that area, and the normal saliva provides another electrolyte at the occlusal surface. Therefore, electrolytic corrosion occurs with preferential attack of

the metal surface occurring underneath the layer of food debris<sup>1,3,4</sup>.

Corrosion of metals, production of the corrosion products, metallic ion release in human body, and the interaction between metals and human body are the factors that determine biocompatibility of metals and alloys<sup>5</sup>. Biocompatibility of metals and alloys is primarily related to their corrosion behavior. If an alloy corrodes more, it releases more of its elements into the mouth and increases the risk of unfavorable reactions in oral tissues. These unwanted reactions include unpleasant taste, irritation, allergy and other reactions<sup>6</sup>.

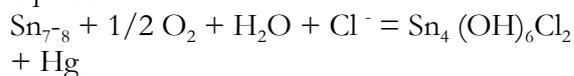
### **Corrosion of Dental Amalgam**

Dental amalgam galvanically corrodes in mouth. The likelihood of galvanic corrosion increases if two phases are present in a metal. Dental amalgams always have more than two phases, and they also exist in a corrosive environment, the oral cavity. Therefore, amalgams corrode and eventually fail. The clinical problem is that corrosion often occurs below the surface of restorations. Assessing the status of an amalgam restoration for internal corrosion is beyond current clinical diagnostic tools and techniques. Instead, alleged recurrent decay is the dominant reason for replacing amalgam restorations<sup>7</sup>.

Amalgam restorations often tarnish and corrode in oral environment. The degree of tarnish and the resulting discoloration appear to be very dependent upon every individual's oral environment and to a certain extent, upon the particular alloy employed. Electrochemical studies indicate that some passivation offering partial protection against further corrosion, occurs as a result of the tarnish process<sup>8</sup>. Active corrosion of a newly placed amalgam comes about in the interface between the tooth and the restoration. The empty space permits the microleakage of electrolytes and a concentration cell (crevice corrosion) process results. The build-up of corrosion products gradually seals this space, making dental amalgam a self-sealing restoration<sup>8</sup>.

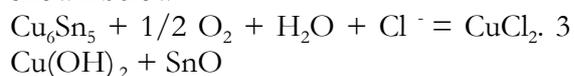
Because of their different chemical compositions, the different phases of an amalgam have different corrosion potentials. Electrochemical measurements on pure phases have shown that the  $\text{Ag}_2\text{Hg}_3$  phase has the highest corrosion resistance, followed by  $\text{Ag}_3\text{Sn}$ ,  $\text{Ag}_3\text{Cu}_2$ ,  $\text{Cu}_3\text{Sn}$ ,  $\text{Cu}_6\text{Sn}_5$ , and  $\text{Sn}_{7-8}\text{Hg}$ . The following compounds have been identified on dental amalgams in patients:  $\text{SnO}$ ,  $\text{SnO}_2$ ,  $\text{Sn}_4(\text{OH})_6\text{Cl}_2$ ,  $\text{Cu}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ ,  $\text{CuCl}$ ,  $\text{CuSCN}$  and  $\text{AgSCN}$ <sup>9</sup>.

In a low-copper amalgam system, the most corrodible phase is the tin-mercury, or  $\gamma_2$  phase. Even though a relatively small portion (11% to 13%) of the amalgam mass consists of the  $\gamma_2$  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  $\gamma$  nor the  $\gamma_1$  phase is corroded as easily. Corrosion results in the formation of tin oxychloride from the tin in the  $\gamma_2$  and also releases mercury, as shown in the following equation:



The reaction of the released mercury with unreacted  $\gamma$  can produce additional  $\gamma_1$  and  $\gamma_2$ <sup>9,10</sup>.

The high copper amalgam alloys do not have any  $\gamma_2$  phase in the final set mass. The  $\eta$  phase formed with high copper alloys shows better corrosion resistance. However,  $\eta$  is the least corrosion resistant phase in high copper amalgams, and a corrosion product,  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ , has been associated with storage of amalgams in synthetic saliva, as shown below:



Phosphate buffer solutions inhibit the corrosion process, thus saliva may provide some protection for dental amalgams against corrosion<sup>9,10</sup>.

### The significance of dental amalgam corrosion

Corrosion of dental amalgam can cause galvanism and galvanic action besides the damaging of restorative metal<sup>1, 3</sup>. The galvanic shock is well known in dentistry

and the effect of galvanic current on the patient has been discussed<sup>2</sup>. The postoperative pain due to galvanic shock can be a real source of discomfort to an occasional patient<sup>2, 3</sup>. The ion release as a result of corrosion is more important and discussion about this matter has been continued<sup>5</sup>.

Prolonged attempts to evaluate and determine dental amalgam corrosion have been made during recent decades and the results have been reported<sup>11-14</sup>. Prominent successes have been obtained about improvement of amalgam corrosion resistance and optimizing amalgam corrosion behavior<sup>15</sup>. Research and efforts have continued and especially most attention was concentrated on effects of mercury on the human body and dental amalgam biocompatibility during the last decade<sup>16-24</sup>.

Mercury used in dental amalgams, however, raises concerns about its biological toxicity and environmental hazard<sup>25</sup>. Although in use for more than 150 years, dental amalgam has been suspected more or less vigorously as a dental restoration material due to its alleged health hazard. Humans are exposed to mercury and other main dental metals (Ag, Sn, Cu, and Zn) via vapor, corrosion products in swallowed saliva, and direct absorption into blood from oral mucosa. Dental amalgam fillings are the most important source of mercury exposure in general population. Local, and in some instances, systemic hypersensitivity reactions to dental amalgam metals, especially mercury, occur with a low incidence among amalgam bearers. Experimental and clinical data strongly indicate that these and other sub-clinical systemic adverse immunological reactions to dental amalgam in humans are linked to certain MHC genotypes, and affect only a small number of exposed individuals<sup>26</sup>.

The presence of amalgam fillings does not appear to affect general health of patients. In summary, it can be stated that epidemiological studies of amalgam bearers have not detected increased incidence of cancer, cardiovascular disease, diabetes, early death or subjectively reported ailments. Furthermore there is no evidence to support

the contention that mercury exposure from amalgam filling could cause neurological disease, multiple sclerosis, motor neuron disease, Alzheimer's disease, Parkinson's disease, chronic fatigue syndrome, renal disease, immunological dysfunction, effects on the fetus, increased antibiotic resistance, and adverse effects on general health<sup>21</sup>.

It has been suggested that the use of amalgams should be discontinued but some<sup>27</sup> believe that amalgam restorations are quite safe. Amalgam restorations will continue to be, until esthetic can match amalgam's longevity, ease of placement, and versatility<sup>10</sup>.

Concerns have been expressed over toxicity of dental amalgam, in particular with respect to marginal fracture, surface degradation, corrosion, release of corrosion products (particularly mercury) and biocompatibility<sup>28</sup>.

Many attempts have been made in order to evaluate amalgam corrosion behavior. Various types of tests and experimental methods have been used to determine the corrosion behavior of commercial amalgams and the results have been reported<sup>29-31</sup>. Evaluation of tarnish in dental amalgams has been performed<sup>32</sup> and immersion tests have been used for determining the mercury ion release values<sup>33</sup>. One of the most important tests for evaluating amalgam corrosion behavior is electrochemical test and many studies were done with this method<sup>34-37</sup> since it was proved that the electrochemical tests are useful, valid and reliable<sup>28</sup>.

In vivo tests and clinical studies have been utilized to evaluate the corrosion, tarnish, and marginal degradation of dental amalgam restorations<sup>38,39</sup> and the correlation between the number of amalgam surfaces and mercury levels in plasma and urine<sup>39</sup>.

Researchers have studied the mercury vaporization from corroded dental amalgam, the release of mercury and the release of mercury vapor from amalgam restorations<sup>40-42</sup>. Concerns have been expressed over the relation of oral mucosal lesions and amalgam restoration<sup>43</sup>, and mercury-specific lymphocytes<sup>44</sup>.

It has been reported that dental amalgam fillings are free of toxic reactions on patients<sup>16</sup>

and allergic contact eczema observed in a few individuals is the only problem in connection with the use of amalgam filling<sup>17</sup>. On the other hand, since the toxicological consequences of exposure to mercury from dental amalgam is a matter of debate in several countries, researchers have tried to obtain data on mercury concentrations in saliva and feces before and after removal of dental amalgam fillings<sup>18</sup>. Before removal, the median mercury concentration in feces was more than 10 times higher than samples from an amalgam free reference group consisting of 10 individuals. Sixty days after removal, the median mercury concentration was still slightly higher than in samples from the reference group. It was concluded that amalgam fillings are a significant source of mercury in saliva and feces<sup>18</sup>.

Health risks from amalgam filling are a subject of controversy. In Germany, it is not advised to use amalgam filling during breast-feeding<sup>22</sup>. The concentration of mercury in human breast milk collected immediately after birth showed a significant association with the number of amalgam fillings as well as with the frequency of meals. Urine mercury concentration correlated with the number of amalgam fillings and amalgam surfaces. In the breast milk after 2 months of lactation, the concentrations were lower compared with the first sample range and were positively associated with the fish consumption but no longer with the number of the amalgam fillings. Accordingly, additional exposure to mercury of breast-fed babies from maternal amalgam fillings is of minor importance compared to maternal fish consumption<sup>22</sup>.

For high copper amalgam, the release of elements increased with time, except for Cu and Sn in the solution with 100 mM phosphate, indicating that phosphate inhibits corrosion of Cu-Sn phases. Release of corrosion products from the high copper amalgam was more dependent on the presence of phosphate than the conventional amalgam<sup>33</sup>.

During recent decades, the use of dental amalgam has been discussed with respect to potentially toxic effects of mercury

component<sup>17</sup>. Therefore, it has been necessary to study more about the dental amalgam corrosion and its biocompatibility. Many researches have been performed in order to obtain more data about the tarnish, corrosion behavior, biocompatibility, and characteristics of dental amalgam all over the world and in Iran<sup>45-60</sup>.

It was shown that the degree of tarnish and the resulting discoloration of three commercial dental amalgams used in Iran, were dependent on parameters such as individual's oral environment, oral hygiene, position of the restoration, clinical performance, and to a certain extent, on the type of commercial dental amalgam<sup>4, 47, 48</sup>. Tarnish and corrosion of three commercial dental amalgams used in Iran namely Sybraloy, Cinaalloy, and SolilaNova, were investigated and evaluated by utilizing *in vitro* tests. The corrosion and dissolution rate of the three commercial dental amalgams were studied in 0.9 wt % NaCl solution, artificial saliva and Ringer's solution by Potentiodynamic polarization technique. The corrosion potential and the corrosion current density of each type of commercial amalgam were found to be affected by the nature of electrolyte, as well as the pre-immersion time. However, the order of corrosion potential and corrosion current density of the three commercial dental amalgams examined, were found to be independent of the type of electrolyte<sup>47-51</sup>.

The mercury release from each type of commercial amalgams into sodium chloride, sodium sulfide in long-term testing was not significant. On the other hand, the mercury release from each type of commercial amalgams into artificial saliva solution in short-term test (the initial mercury release) was considerably significant<sup>4, 52-54</sup>.

Four different types of commercial amalgam alloys with various chemical compositions and particle shapes (lathe cut, spherical, spheroids) namely; Sybraloy, Oralloy, Cinaalloy, and Cinalux were studied. Adequate samples of each type of the amalgams were prepared. After triturating and condensation, the samples of each type were divided into three groups and using

one of the following three procedures; carving, carving-burnishing, carving-burnishing-polishing. Structural characterization techniques including SEM were used to investigate the surface morphology of amalgam samples<sup>55-57</sup>. Electrochemical potentiodynamic tests were performed in physiological solution in order to determine the corrosion behavior of different amalgams as an indication of biocompatibility<sup>58-60</sup>.

It was shown that shape of particles and clinical procedures could affect the final surface roughness of each type of commercial dental amalgam. There was a statistically significant difference between the mean surface roughnesses of three different groups of each type of amalgam. The carved group of each type of dental amalgam showed the most surface roughness while the carved-burnished-polished group had the most surface smoothness<sup>55,57</sup>. The results showed statistically significant differences between the mean corrosion current density values of the three different groups of each type of the commercial amalgam (Figures 1 and, 2). The polished group of each type of commercial amalgam possesses the lowest corrosion current density and the carved group shows the highest corrosion current density. This trend was not affected by the chemical composition of commercial amalgams. The carved Sybraloy possesses the lowest corrosion current density compared to the other three types of amalgams. The carved group of the Cinaalloy also possesses the highest corrosion current density (Figure 3). The similar trend can be observed for the carved-burnished and the carved-burnished-polished group of four brands of amalgam (Figure 4). It was concluded that the clinical operations and procedures could be effective on tarnish and corrosion of amalgam besides surface plaque accumulation and recurrence of tooth caries<sup>57-60</sup>.

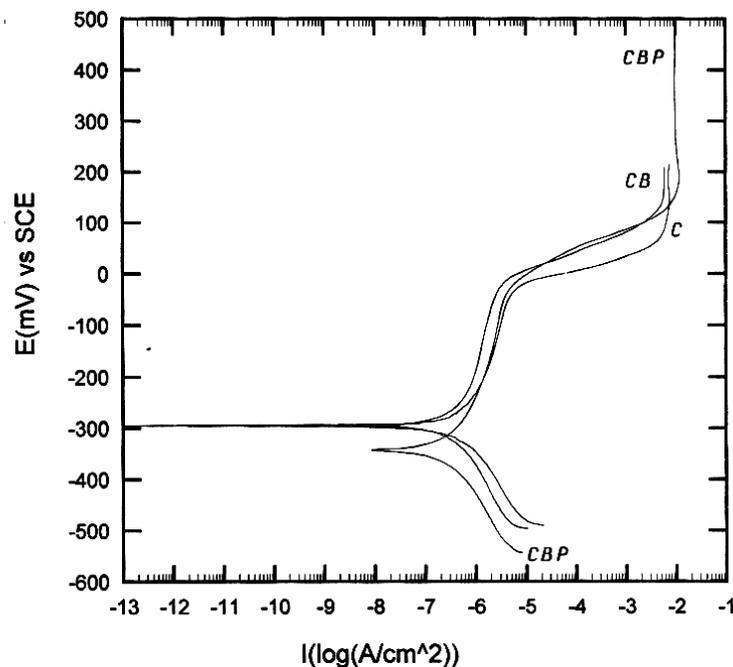
## Conclusion

Today's amalgams are much more durable and reliable than what was available in 1895

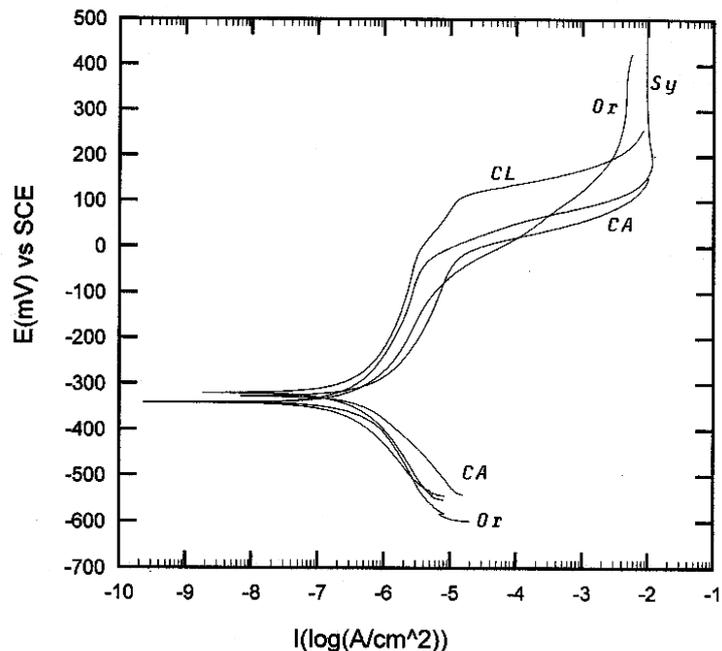
when Black began his studies. In fact, they are now more durable than they used to be 30 years ago.

Although in use for more than 150 years, dental amalgam has been suspected more or less vigorously as a dental restoration material due to its alleged health hazard. It considers the possible toxic and allergic effects, which could occur as a result of exposure to mercury from dental amalgam. The main toxic effects are thought to be neurotoxicity, kidney dysfunction, reduced immunocompetence, effects on oral and intestinal bacterial flora, fetal and birth effects and effects on general health.

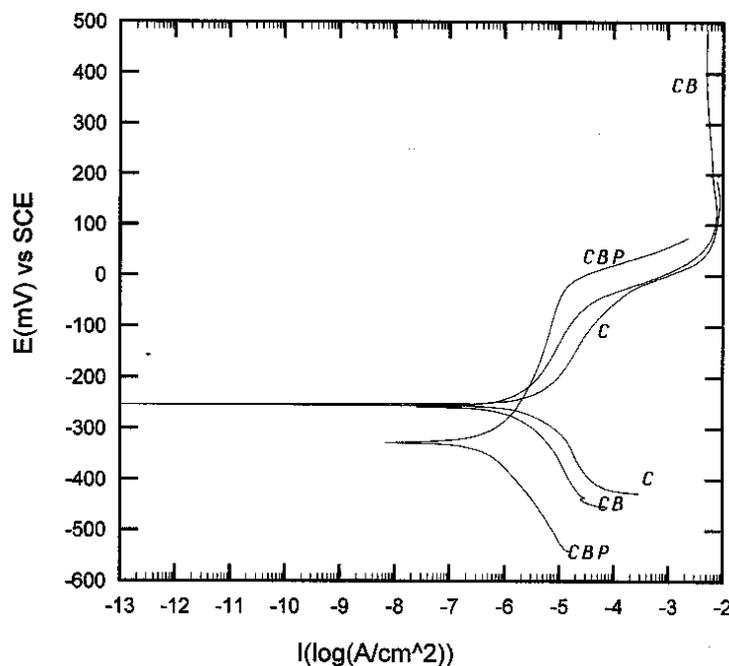
In general, like X-rays or fluoride treatments, the therapeutic advantages of dental amalgams seem to outweigh the relatively small risk of adverse effects. Banning mercury-based fillings and removing them would not only result in serious losses of dentition, but substitution of an alternate material will carry the burden of proving that the substitute does not contain potentially toxic ingredients at perhaps the same or greater level of risk as well.



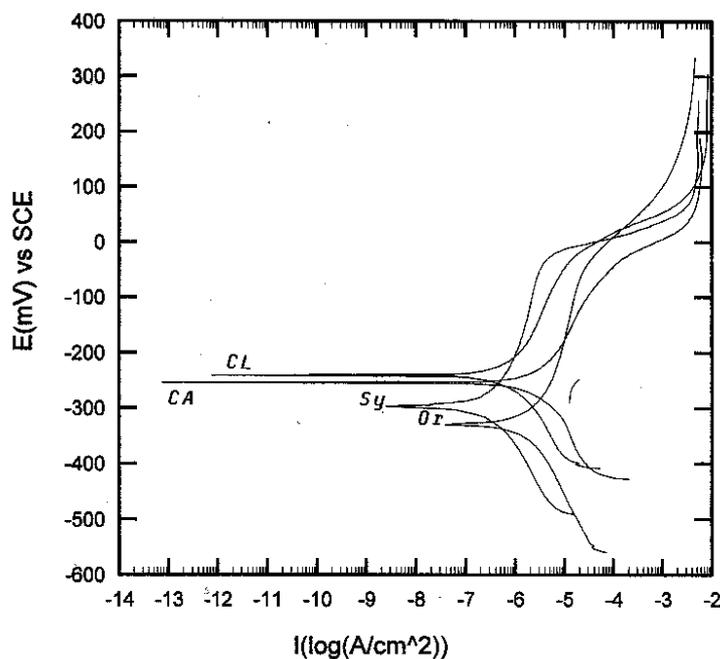
**Figure 1.** Potentiodynamic polarization curves of the carved (C), carved-burnished (CB), and carved-burnished-polished (CBP) groups of the Sybraloy amalgam in the normal saline solution at 37 °C.



**Figure 2.** Potentiodynamic polarization curves of the carved (C), carved-burnished (CB), and carved-burnished-polished (CBP) groups of the Cinalloy amalgam in the normal saline solution at 37 °C.



**Figure 3.** Potentiodynamic polarization curves of the carved group of four types of commercial amalgams in the normal saline solution at 37 °C.



**Figure 4.** Potentiodynamic polarization curves of the carved-burnished-polished group of four types of amalgams in the normal saline solution at 37 °C.

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