Corrosion behavior of dental amalgams and their phases was investigated by means of an electrochemical method and surface analysis by electron probe X-ray microanalyzer. The tin and tin-containing intermetallic compounds had an anodic and two cathodic current peaks with nearly identical potentials. The $\beta_2$ phase had the highest peak current. Polarization curves of the dental amalgams showed two anodic current peaks (1a and 2a) and three or four cathodic current peaks in the range of potential from $-1.5V$ to $+0.5V$.

On the basis of the equilibrium potential, the peaks 1a and 1c were thought to be due to the formation and reduction of divalent tin salt. The peaks 2a and 2c were considered to be due to the formation and reduction of quadra-valent tin salt. A Sn-Cl rich cluster was observed on the sample of the conventional amalgam after the anodic polarization.

Key words: Corrosion, Amalgam, NaCl.

INTRODUCTION

Secondary caries are frequently associated with marginal fractures of amalgam restorations. One of the important causes appears to be the corrosion of dental amalgam restorations. The purpose of this study was to elucidate the mechanism of corrosion of dental amalgams. Such corrosion is known to be an electrochemical reaction; therefore, we study the electrochemical reaction of the pure metals constituting dental amalgams and their intermetallic compounds using a potentiostatic technique.

MATERIALS AND METHODS

The specimen electrodes used were pure Ag, Sn and Cu metals. For dental amalgams we used a conventional amalgam* and a high copper amalgam**. In addition, we used four component phases, i.e. Ag-Hg, Sn-Hg, Ag-Sn, Cu-Sn compounds. These intermetallic compounds were prepared by mixing the required amount of pure component metals, followed by melting and homogenizing in vacuum-sealed quartz tubes. X-ray diffraction analysis identified these alloys with the respective intermetallic compounds.

The dental amalgams were prepared by mechanical trituration according to the manufacture's instruction. The electrodes were ground with emery paper and polished with

* Hi-atomic M.G.C. Dental Industrial Corp., Tokyo, Japan
** Dialloy G.C. Dental Industrial Corp., Tokyo, Japan
aluminum paste of a diameter of 0.5 μm and then rinsed with distilled water. The electrolytic cell that we used was of 80 ml capacity and was maintained at 37°C. It had a capillary connected to an Ag/AgCl reference electrode. The electrolyte was 0.9% NaCl solution made of pure NaCl and doubly distilled water. It was deoxygenated for one day prior to each measurement.

Electrochemical polarization was carried out using a potentiostat*** with a function generator that provided a potential sweep at the rate of 17 mV/second. The specimen surfaces, before and after the polarization, were examined using an electron probe X-ray microanalyzer (EPMA).

RESULTS AND DISCUSSION

Figure 1 shows the polarization curves for the pure metals, Ag, Sn, Cu. The anodic current began to increase rapidly at -0.1 V for copper and at +0.05 V for silver. Tin showed an anodic current peak at -0.8 V and a current rise at -0.5 V. From the theoretical equilibrium potential of this metal, it appeared that this peak corresponds to the oxidization of tin to divalent tin salt and that the current rise at -0.5 V corresponds to the oxidation of divalent tin salt to quadra-valent tin salt.

Figure 2 shows the polarization curves of the intermetallic compounds. The Ag₅Hg₃ (γ₁ phase) had the anodic peak at +0.25 V, whereas the curve of Sn₄Hg (γ₂ phase) displayed an anodic peak at -0.8 V, followed by a current rise at -0.5 V. The curves of Ag₃Sn (γ phase)

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*** HP-E500 Nichia Keiki Corp., Tokyo, Japan

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Fig. 1  Polarization curves for Ag, Sn, Cu in 0.9% NaCl solution.
and Cu₅Sn₅ (η' phase) showed an anodic current peak at the same potential, but the anodic peak current of η' phase was higher than that of γ phase. Tin containing intermetallic compounds, γ, η', γ₂ had similar polarization curves, but the anodic peak currents of γ₂ phase were higher than those of γ, η' phases.

Figure 3 shows the polarization curves for a conventional amalgam and a high copper amalgam. The left figure is the polarization curves of a conventional amalgam and a high copper amalgam.
Fig. 4 EPMA images of a conventional amalgam before polarization.
Fig. 5  EPMA images of a conventional amalgam after polarization.
Fig. 6 EPMA images of a high copper amalgam before polarization.
Fig. 7 EPMA images of a high copper amalgam after polarization.
copper amalgam. They showed two anodic current peak at $-0.85 \, \text{V}$ and $-0.5 \, \text{V}$, followed by a current rise at $0 \, \text{V}$. Both anodic current peaks of conventional amalgam were higher than those of the high copper amalgam. Also the former had four cathodic current peaks and the latter three.

The right figure shows the polarization curve obtained by reversing the direction of potential sweep at respective points beyond the peak. The cathodic current peaks, $1c$ and $2c$ corresponded to anodic peaks, $1a$ and $2a$, respectively, therefor, showing the reduction of the oxide formed at the respective anodic peak, $1a$ and $2a$. The other peaks $3c$ and $4c$ were caused by the reduction of the oxide formed at potential higher than $0 \, \text{V}$.

Figure 4 shows EPMA images of a conventional amalgam before polarization. The $\gamma$ phase, $\gamma_1$ phase and $\gamma_2$ phase are seen. Figure 5 shows EPMA images of a conventional amalgam after polarization. The left on the top shows a secondary electron scanning image in which a Sn-Cl rich cluster resembled that found by Marshal et al\textsuperscript{12}). This cluster can be identified with a tin chloride salt, as easily from the other photograph of element distribution map. These photographs also suggested the presence of corrosion products on the exposed surface.

Figure 6 shows EPMA images of a high copper amalgam before polarization. X-ray diffraction revealed no $\gamma_2$ phase. Figure 7 shows EPMA images of a high copper amalgam after polarization. No Sn-Cl rich cluster was detected.

CONCLUSION

1) The tin and tin-containing intermetallic compounds had one anodic and two cathodic current peaks appearing with nearly identical potentials. The $\gamma_2$ phase had the highest peak current.

2) Polarization curves of the dental amalgam showed two anodic current peaks and three or four cathodic current peaks in the range of potential from $-1.5 \, \text{V}$ to $+0.5 \, \text{V}$.

3) On the basis of the equilibrium potential, the peaks $1a$ and $1c$ were thought to be due to the formation and reduction of divalent tin salt. The peaks $2a$ and $2c$ were thought to be due to the formation and reduction of quadra-valent tin salt.

4) A Sn-Cl rich cluster was observed on the corroded sample of the conventional amalgam.

REFERENCE


歯科用アマルガムとその構成相の生理食塩水中での腐食挙動に関する研究

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従来型及び高鋼型アマルガムとそれらの構成相の0.9％食塩水中での腐食挙動を，電気化学的方法によって検討した。

電位走査法によって電位一電流曲線を求める結果，Sn，Sn₄Hg，Ag₃Sn，Cu₆Sn₅では，同じ電位付近に，1つのアノードビーグと2つのカソードビーグがみられ

有機セメントの歯質への接着性に関する研究
その2　象牙質への接着力に与える各種のモーダントの効果について

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最良の表面処理システムを開発する目的で，グラスアイオノマーセメントと，クレンザー及び各種のモーダントを用いて処理した象牙質の接着力を測定した。また上記の結果から選ばれた表面処理システムが，他の5種のセメントの接着力に与える影響についても検討を加えた。その結果，37度水に1日浸漬したもの後の接着力は，0.5摩ルのマレイン酸とFe(III)イオンを含む3種のモーダントを用いると増加し，中でもモーダントに10％塩化第二鉄，10％硫酸第二鉄アンモニウムを用いると特に大きく増加した。また，カルボキシレートセメントやグラスアイオノマーセメントのような，ポリカルボン酸をベースにした有機セメントの象牙質への接着力は，0.5モルマレイン酸と10％硫酸第二鉄アンモニウムによる表面処理によって大きく増強されたが，2種のレジンセメントについては，増強効果はなかった。