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Potentiostatic Corrosion Test for Dental Amalgams

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Summary

The aim of this study was to examine the validity of a test method (report from ISO/TC meeting in London, October 1998, document N55) for the corrosion resistance of amalgam, considered for adoption as ISO (International Organization for Standardization) test. The corrosion resistance of six types of amalgam was evaluated using the proposed potentiostatic test (N55). The test procedure (N55) was found to be relatively simple and provide reproducible results. Therefore the proposed potentiostatic test can be justified as a standard test of corrosion resistance for dental amalgams.

Introduction

The ISO (International Organization for Standardization) has evaluated standard test methods for dental materials and devices in special working groups. One of the groups has considered development of a standard test method for the corrosion resistance of dental amalgam. In Japan, the use of dental amalgam is decreasing rapidly in view of the concerns regarding toxicity of mercury, which is a component element of amalgam. The health risk due to the mercury released from amalgam has not been substantiated, however. Dental amalgam continues to be used throughout the world and a standard test of the corrosion resistance is desirable.

The working group ISO TC106/SC1/WG7 (alloy for dental amalgam) has discussed a test of the corrosion resistance for dental amalgam for several years. Several tests have been proposed, and some round robin testing has been performed. The test method, which was the subject of this study (report from ISO/TC meeting in London, October 1998 document N55), was proposed to ISO by Dr. M. Marek in 1998. The test is based on an electrochemical polarization method, and the corrosion resistance is evaluated according to the anodic charge passed during the test period at a constant potential. The test was subjected to round robin testing at five laboratories in four countries, which was a prerequisite for the acceptance of the method.

The aim of this study was to examine the reproducibility of the proposed test method (N55). The

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corrosion resistance of six kinds of amalgam was evaluated using the potentiostatic test procedure.

Materials and Methods

Specimen preparation

The chemical composition of the alloy powders used to prepare the six types of tested commercial amalgams is shown in Table 1. Amalcap Plus (Vivadent Lot A532292) and Spherical D (Shofu Lot 119826) are γ_2-free and zinc-free dispersed phase amalgams . Dispersalloy (Dentsply Lot 971111F) is also a dispersed phase alloy. Vivacap (Vivadent Lot A06359) and Tytin (Kerr Lot 8-1008) are single component alloys. F400 (SDI Lot 711262) is a micrograin, lathe-cut alloy. The powders were triturated and condensed according to ANSI/ADA Specification No.1 to produce standard specimens (diameter 4mm). After aging for two weeks at room temperature the specimens were embedded in epoxy and prepared as working electrodes. The exposed end of the specimen was wet-ground to 600 grit or FEPA #1200 and washed with distilled water.

Table 1 : Chemical Composition of Alloy Powder (wt. %)

Alloy	Code	Ag	Sn	Cu	Zn
Tytin	TYT	60	28	12	-
Amalcap Plus	AMP	70.1	18	11.9	-
Dispersalloy	DIA	69.3	17.9	11.8	1
Spherical D	SPD	59.5	27.5	13	-
Vivacap	VIC	46.5	30	23.5	-
F400	F400	70	26	3.5	0.5

Corrosion test cell

A three-electrode corrosion cell was used, holding the specimen (working electrode), a reference electrode (0.1M KCl Ag/AgCl) probe, and an inert counter-electrode (platinum wire). The cell was maintained at 37±0.5℃ by means of a temperature-controlled bath. The electrolyte was an aqueous solution of 0.9% NaCl by weight, and the solution volume was 500 ml.

Test procedure

The cell was filled with the electrolyte, which remained open to the atmosphere, and maintained at 37±0.5℃. The specimen (working electrode) was inserted into the cell and the three electrodes were connected to the potentiostat. During a waiting time of 10minutes the specimen was under open circuit conditions, and the potential was recorded at the end of the 10-minute exposure period. The potentiostat (SEIKO EG&G Model 283, Corrosion software Model 252/352) was set to the potentiostatic mode, and the control potential and time were adjusted. The control potential was-0.047V, to provide the specified working electrode potential of 0.0V vs. SCE (0.242V vs. SHE). The time was set at 24 hours. The potential was applied and the current was measured and recorded.

Results and Discussion

Figs.1-6 show the potentiostatic curves for each amalgam. These curves revealed a sharp initial current peak, the current then decreasing to an almost constant value. The integrated current density (anodic charge, coulombs. cm^{-2}) is the corrosion index C_{24}. The stabilized value of the current affected the corrosion index C_{24} more than the initial sharp peak value. Since the anodic charge is proportional to the mass of the metal dissolved or converted into corrosion products according to the Faraday's law, the value of the corrosion index C_{24} corresponds to the amount of the corrosion damage. The larger the corrosion index C_{24}, the lower is the corrosion resistance of the tested dental amalgam in 0.9% NaCl aqueous solution.

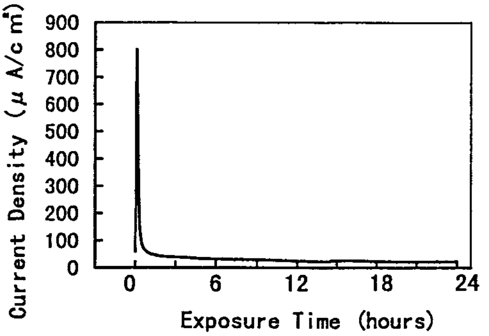

Fig.1 : Potentiostatic curve (current density as a function of exposure time) in 0.9% NaCl at 37℃ for Tytin (TYT).

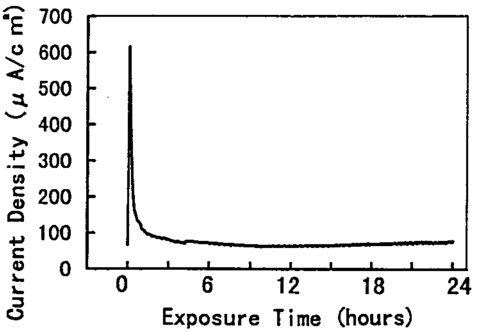

Fig.2 : Potentiostatic curve (current density as a function of exposure time) in 0.9% NaCl at 37℃ for Amalcap Plus (AMP).

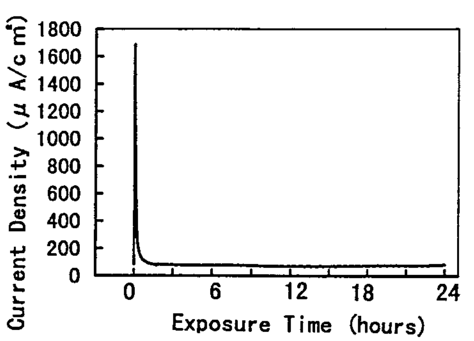

Fig.3 : Potentiostatic curve(current density as a function of exposure time)in 0.9% NaCl at 37℃ for Dispersalloy (DIA).

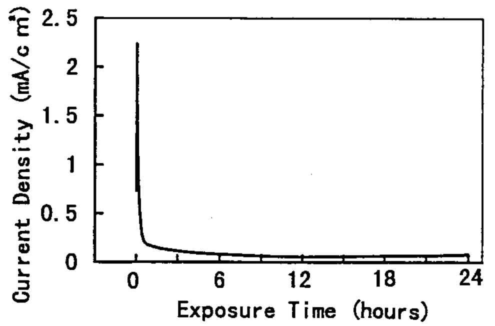

Fig.4 : Potentiostatic curve (current density as a function of exposure time) in 0.9% NaCl at 37℃ for Spherical D (SPD).

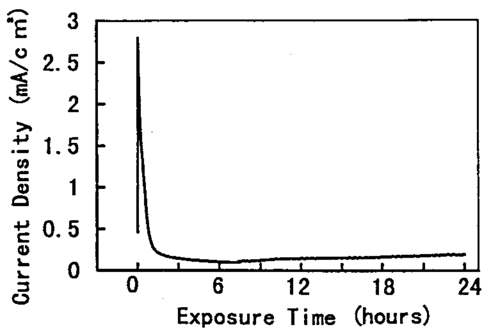

Fig.5 : Potentiostatic curve (current density as a function of exposure time) in 0.9% NaCl at 37℃ for Vivacap (VIC).

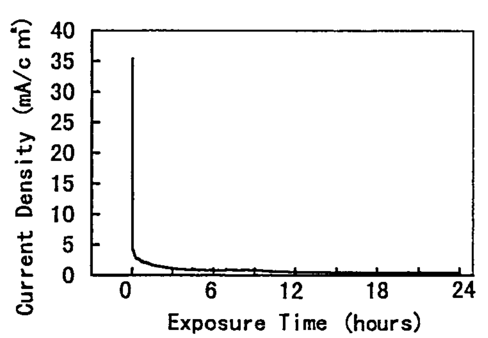

Fig.6 : Potentiostatic curve (current density as a function of exposure time) in 0.9% NaCl at 37℃ for F 400 (F400).

Fig.7 shows the measured values of the corrosion index C_{24} for the tested amalgams. When the amalgam contains the γ_2 phase, like F400 does, the test results in a large value of the corrosion index C_{24}. The corrosion resistance of F400 was lowest of the tested amalgams. This result is consistent with the corrosion data reported in previous studies, which showed that the γ_2 phase was the most corrosion-prone phase in the structure of low-copper amalgams,[1-3] and that γ_2-containing amalgams exhibited corrosion resistance inferior to γ_2-free amalgams.[1] Tytin, a high-copper, γ_2- free amalgam, exhibited the smallest value of the corrosion index C_{24}, indicating that the corrosion resistance of Tytin was the highest of the tested amalgams, also in agreement with previous reports[1,4]. The results for the other amalgams were intermediate between those for F400 and Tytin, but generally superior to those for F400. There was no statistically significant difference between the results for the three dispersed phase amalgams (Amalcap Plus, Shofu Spherical D, and Dispersalloy), indicating similar corrosion performance. Vivacap, a high-copper, single composition alloy amalgam, showed results significantly inferior to Tytin, the other high-copper, single composition alloy amalgam, and the highest value of the corrosion index C_{24} among the high-copper amalgams. The difference may be attributed to the very high copper content of Vivacap. Copper combines with tin to form the phase η' (Cu_6Sn_5) which, in the absence of the γ_2 phase, is the most corrosion-prone of the structural phases in high-copper amalgams.[1]

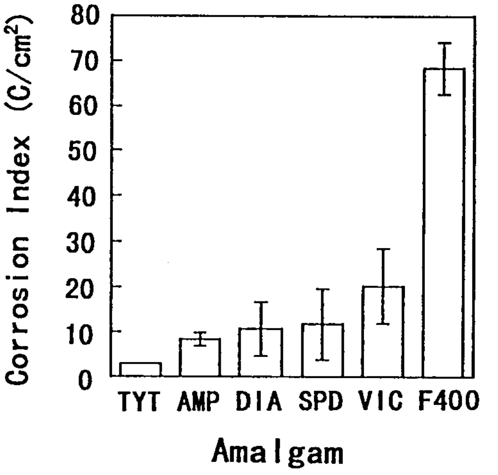

Fig.7 : Bar graph comparing the corrosion indices C_{24} for six kinds of dental amalgams in0.9% NaCl at 37℃. Data bars represent means (n=5), error bars represent their standard deviation.

The corrosion index C_{24}, obtained by means of a potentiostatic method, was successfully used to rank six kinds of dental amalgams with respect to corrosion resistance. The potentiostatic test results were in good agreement with the results of the ISO immersion test, in which the amounts of elements dissolved from the alloys were determined by solution analysis (N59)[5]. The potentiostatic test procedure was substantially simpler than the immersion and analytical procedures used in the ISO immersion test. A potentiostatic test also can be applied to evaluate the corrosion resistance of other dental alloys. However, the test cannot be applied without modification to compare alloys of substantially different composition. Electrochemical dissolution of different elements depends on their thermodynamic and kinetic parameters, and a potentiostatic exposure at the same potential would accelerate differently dissolution of different elements.

Standard test methods should involve a simple procedure, and the principle must be theoretically sound. The evaluated test procedure is relatively simple and does not require special skills of the operator or unusually sophisticated electrochemical or analytical instrumentation. The interpretation of the results (corrosion index C_{24}) is straightforward and based on a sound electrochemical theory. Therefore, a potentiostatic test can be justified as a standard test of corrosion resistance for dental amalgams.

References

1) Marek M (1983) Treatise on materials science and technology, "Corrosion : Aqueous processes and passive films," : 331–44. Academic Press, London.
2) Guthrow CE, Johnson LW, Lawless KR (1967). Corrosion of dental amalgam and its component phases. J Dent Res **46** : 1372–381.
3) Horasawa N, Nakajima H, Ferracane JL, Takahashi S, Okabe T (1996) Cyclic voltammetry of dental amalgams. Dent Mater **12** : 154–60.
4) Marek M (1990) The effect of tin on the corrosion behavior of the Ag–Hg phase of dental amalgam and dissolution of mercury. J Dent Res **69** : 1786–90.
5) ISO (1998) Dental materials–alloy for dental amalgam. ISO/TC106/SC I/WG7 draft N59. International Organization for Standardization, London.

抄録：ポテンショスタティック法による歯科用アマルガムの耐食性試験

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本研究は，アマルガムの耐食性評価試験（report from ISO/TC meeting in London, October 1998 document N55）法として，ISOにおいて検討された試験方法の1つについて，規格試験方法としての妥当性を検討した．検討は，6種類のアマルガムについてISO規格試験方法として申請された，ポテンショスタティック法（N55）を用いて耐食性を評価して行った．その結果この試験方法（N55）は，比較的簡便な手順で，結果の再現性も良好であった．よってポテンショスタティック試験方法は，歯科用アマルガムの耐食性評価の規格試験方法として，適当であると言える．