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STRUCTURE AND CORROSION OF DENTAL AMALGAMS

by

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INTRODUCTION

Numerous studies (*Schoonover & Souder*, 1941; *Wagner*, 1962; *Jørgensen*, 1965; *Guthrow et al.*, 1967; *Kyselova et al.*, 1968) have demonstrated unquestionably that the corrosion of dental standard amalgams is characterized by an anodic attack on the γ_2 phase of the amalgams. This corrosion releases the γ_2 phase tin in the form of tin ions, the mercury being released as metallic mercury and absorbed by the γ and γ_1 phase of the amalgam. The tin ions are often deposited as solid products of corrosion on the surface of the amalgam and can thus in oral conditions give rise to unfortunate hygienic consequences on the surface of the filling (»periferal surface corrosion») with gingival implications; the absorbed mercury can cause the edges of the amalgam filling to bend, thus becoming unsupported and subject to possible fracture (*Jørgensen*, 1965). The corrosion of the γ_2 phase is thus a major — possibly the principal — cause of the failure of amalgam fillings.

If the γ_2 grains do not anastomose through the amalgam, their corrosion must halt when all the surface grains have dissolved; at the same time the destructive effects of corrosion will cease. Conversely, if the γ_2 grains do anastomose, it will be possible for corrosion to continue deep into the amalgam — and the destructive effects of the corrosion will correspondingly be more widespread. The purpose of the present work has been to study the degree

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of anastomosis between the individual grains of the γ_2 phase in dental amalgams.

MATERIALS AND METHODS

Materials. A total of 24 different brands of dental amalgam alloy were used in the study. As regards composition and physical properties 22 of these complied with the requirements of F.D.I. Specification no. 1. Of the remaining two brands, one (no. 2, Dispersalloy 400*) met the demands of the Specification as far as physical properties are concerned but not as regards composition because it had a copper content of 12 %; the other (no. 24), which had a tin content of 50 % and a silver content of 47 %, fulfilled the requirements of neither composition nor physical properties. Three of the 22 standard brands were of the spherical type.

Of the 22 brands that met the requirements of the Specification, 7 contained zinc and were not pre-amalgamated (group A), 4 were without zinc and were not pre-amalgamated (group B), 7 contained zinc and were pre-amalgamated (group C), and 4 were without zinc and were pre-amalgamated (group D).

Method of mixing. The brands in groups A and B and brand no. 2 were triturated with 60 % mercury, the brands in group C and D with 55 % mercury and brand no. 24 with 50 % mercury. Trituration was done by a Wig-L-Bug** with a plastic-coated pestle in a plastic capsule; trituration time in every case was 20 seconds plus 2 seconds without pestle.

Method of condensation. The amalgam was condensed in a cylindrical steel die with a diameter of 5.0 mm with the aid of plungers whose diameter was approximately 0.01 mm less than that of the die. Condensation was commenced two minutes after the start of trituration, and lasted for three minutes. Condensation pressure was a constant 40 kp.

Normally the specimens had a length of 10.0 mm ± 0.5 mm; in the experiments with sodium citrate (see below) the length was however only 5.0 mm ± 0.2 mm. The mercury content in specimens from groups A and B was between 43.3 % and 50.3 %, and from groups C and D between 35.9 % and 43.7 %; specimens of brand no. 24, which had a high content of tin, had a mercury content of approximately 22 %. In the case of most brands the standard deviation for the mercury content for 10 specimens was less than 0.5 %. All specimens were at least one week old before being subject to tests.

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* Western Metallurgical Ltd., Edmonton, Canada.

** Crescent Mfg. Co., Chicago, USA.

Chemistry of the corrosion process. In a series of preliminary experiments specimens with their bases ground plane were placed on flat glass plates in a solution of 1 % NaCl at a temperature of 37° C; in addition the solution contained a small quantity of phenolphthalein. It is assumed that under these conditions the oxygen concentration on the bases of the specimens was lower than on the free surfaces. In some experiments any difference in oxygen concentration on the surface of the specimens was eliminated, either by using an oxygen-free NaCl solution or by suspending the specimens in the gelatinized electrolyte solution. The specimens were removed from the electrolyte solutions after 4—8 weeks and investigated immediately.

Metallographic analysis of serial sections of amalgam. Only one of the brands from Group A (True Dentalloy*) was used in this experiment. One specimen was made according to the standard method (final mercury content 47 %) and one was given a much greater mercury content (58 %). After several days the specimens were invested in Palatal** and ground under cold water parallel with their longitudinal axis. The amalgam surfaces, which measured 5 × 10 mm, were then polished with diamond paste A (approx. 7—15 μ) and fine-grained, precipitated diatomite. After the polishing process a central area of each specimen was photographed, enlarged linearly approximately 70 times. Polishing and photographing of the same area was repeated 15 times. Each time polishing was carried out a layer ca. 1 μ thick was removed from the amalgam. When the photographic negatives were printed they were enlarged 5 times. Thus the total enlargement of the photographs was 350 times.

Selective dissolution of the γ_2 phase in sodium citrate. Twelve cylindrical specimens of all standard brands and of Dispersalloy 400 were made according to the general method described in the foregoing; the diameter and height of the specimens was 5 mm. The specimens were thoroughly subjected to vacuum at a residual pressure of 2 Torr in demineralized water in order to eliminate air from any surface defects; specimens were then placed in crystallizing dishes with 250 ml of a 10 % sodium citrate solution at a temperature of 37° C, with their base surfaces resting on a flat glass plate. Each dish contained only two specimens; five dishes containing specimens were allotted to each brand; the remaining two specimens were used for control. Throughout the course of the experiment the level of the solution in the dishes was kept constant by the addition of demineralized water. The thermostat cabinet used in the experiment was kept free of dust. The samples were removed from the citrate solution after 2, 4, 8, 16 and 32 weeks,

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* S. S. White Dental Mfg. Co. (G. B.) Ltd., London.

** Badische Anilin- & Soda-Fabrik AG., Ludwigshafen a. R., Western Germany.

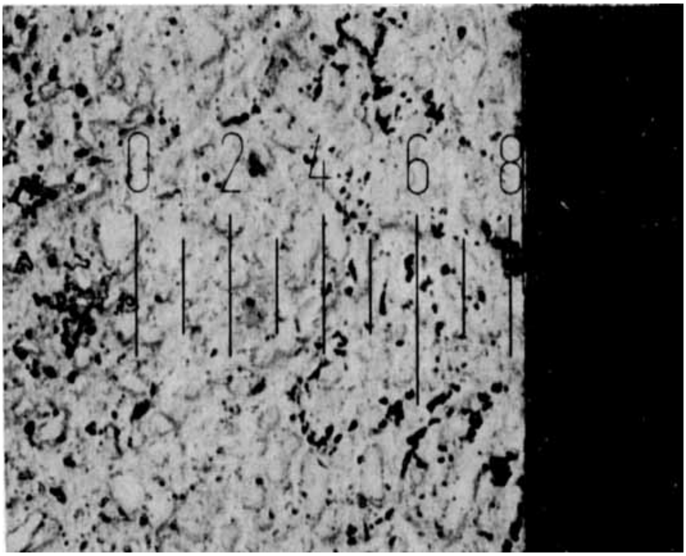

Fig. 1. Measurement of the depth to which the γ_2 phase has dissolved in the sodium citrate solution. The end transverse line of the ocular scale is flush with the periferal part of the first γ_2 grain from the surface of the specimen. ×115.

respectively, cleaned in demineralized water under a vacuum and dried They were then invested in pairs in Palatal, and ground to their centers parallel with their longitudinal axes. The resulting 5×5 mm amalgam surfaces were finally reliefpolished with fine-grain, precipitated diatomite, initially on a rotating and then on a vibrating polishing table (Vibromet*).

The depth of the zone in which the γ_2 phase had been dissolved was measured on all specimens of standard amalgam. The measurements were made in the middle of the side surface and at a distance of 1.5 mm from the top and base on both the right and left side of the specimens. Thus a total of 12 points were measured for each brand and for each period of the respective number of weeks. The depth was measured by means of a measuring microscope and a measuring ocular; the specimen was placed in such a way that the end transverse line of the ocular scale (Fig. 1) was flush with the periferal part of the first γ_2 grain from the surface of the specimen. The distance from the end transverse line to the surface was then read.

RESULTS

Chemistry of the corrosion process. Already a few hours after placing the specimens on the flat glass plate in a 1 % NaCl solution a mild basic reaction

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* Buehler Ltd., Evanston, Illinois, USA.

Fig. 2. Crystalline products of corrosion on the surface of an amalgam. ×40.

was observed around the free surfaces of the specimens. After termination of the experimental period it was observed that all base surfaces were extensively covered by solid corrosion products which were as a rule clearly crystalline (Fig. 2). The metallic base surface sometimes visible between the deposited corrosion products was not as a rule discoloured. The side and top surfaces of the specimens showed no or only few traces of deposited corrosion products; on the other hand these surfaces were frequently darkly discoloured.

A metallographic study of relief-polished, unetched sections of the specimens demonstrated in every instance a *selective dissolution of the* γ_2 *phase* of the amalgams (Fig. 3) to a depth that was to a certain extent proportional to the duration of the period of corrosion but independent of brand, provided that the brand complied with the composition requirements of F.D.I. Specification no. 1. Dissolution of the γ_2 phase had taken place almost exclusively in the base area of the specimen cylinders. Dissolution of the γ_2 phase on side and top surfaces had occurred only in connection with local, relatively rare instances of porosity (Fig. 4). There was thus a good degree of conformity between the localization of deposited corrosion products and the dissolution of the γ_2 phase.

Local porosity occurred more frequently in zinc-free amalgams than in amalgams containing zinc. One of the pre-amalgamated brands also produced

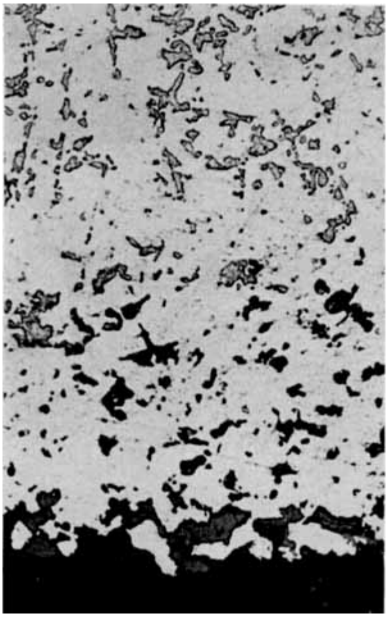

Fig. 3. Section of an amalgam specimen after a corrosion test in a 1 % NaCl solution: the γ_2 phase in the surface layer has dissolved. ×160.

more porous specimens than brands which were not pre-amalgamated and which contained zinc. A study of the structure revealed that this greater degree of porosity was caused by locally inferior amalgamation of the alloy particles. *Brecht-Bergen* & *Loebich* (1934) also demonstrated the significance of the porosity of the amalgam for anodic corrosion.

If the differences in oxygen concentration on the surfaces of the specimens were eliminated standard silver amalgams did not corrode. This was evident both in the experiments with an oxygen-free NaCl solution and in the experiments in which the specimens were suspended in the gelatinized electrolyte solution. With the latter method corrosion could be completely eliminated only if the surface of the specimen was without porosity, which was frequently the case; when local surface porosity was present, corrosion (the depositing of corrosion products, dissolution of the γ_2 phase) could be shown to occur.

The observations described indicate very strongly a galvanic corrosion resulting from differences in concentration of oxygen on the surface of the specimens (cf. *Jørgensen*, 1965). In the corrosion process the base surface of the specimens (with a relatively low oxygen tension) forms the anode, while the side and top surfaces form the cathode.

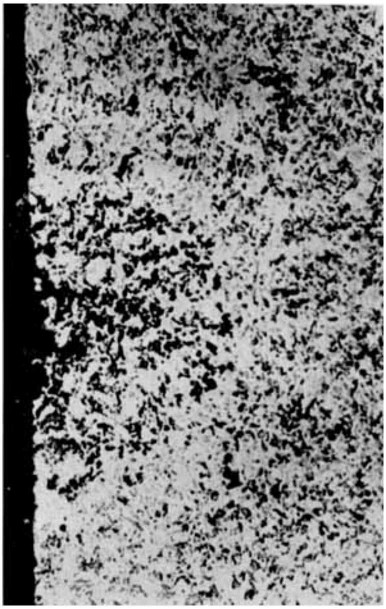

Fig. 4. Corrosion around voids on the side surface of an amalgam specimen made of zinc-free alloy. The γ_2 phase is completely dissolved in the porous area. ×80.

Thus the anode process is: $Sn \rightarrow Sn^{++} + 2e^-$ while the cathode process must be: $2H_2O + O_2 + 4e^- \rightarrow 4OH^-$. The combined corrosion process is thus: $2Sn + 2H_2O + O_2 \rightarrow 2Sn^{++} + 4OH^-$.

The mercury released by the anodic corrosion has been the subject of an earlier study (*Jørgensen*, 1965).

Metallographic examination of serial sections of amalgam. The individual photographs (Fig. 5) did not make it possible to decide to what extent the γ_2 grains anastomose. On the other hand, when a successive comparison was made of photographs of amalgam surfaces with differences in level of approx. 1 μ, *it was possible in the specimen containing most mercury to* identify the individual γ_2 grains from level to level, and to demonstrate anastomosis in different levels among most γ_2 grains (Fig. 6). A corresponding analysis was not possible in the specimen containing only 47 % mercury because of the very small size of the γ_2 grains here.

A study of the structure of well-condensed specimens of the other standard brands containing relatively little mercury showed that the γ_2 grains in all cases were of similar small size as in the well-condensed specimen of True Dentalloy. The method described did not therefore make it possible to arrive at a general solution to the problem of the anastomosis of the γ_2 grains.

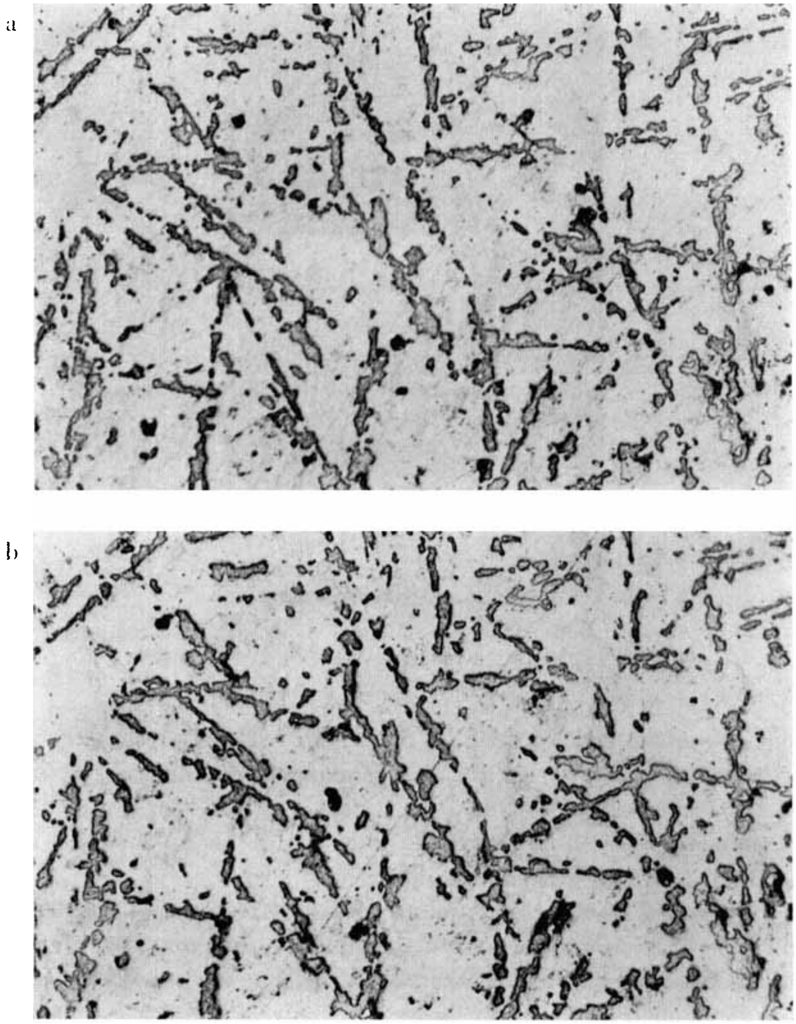

Fig. 5. a. The γ_2 phase in an amalgam with a relatively high mercury content. b, same area, approximately 1 μ deeper into the amalgam surface. ×200.

Selective dissolution of the γ_2 phase in sodium citrate. The microscopic examination of preparations made from standard brands demonstrated in all cases that the dissolution of the γ_2 phase of the amalgam advanced according to the length of time spent in the citrate solution; after 32 weeks dissolution of this phase was complete or almost complete in all brands. *Thus proof was obtained that all γ_2 grains in each of the amalgams of standard alloys tested anastomose with each other.*

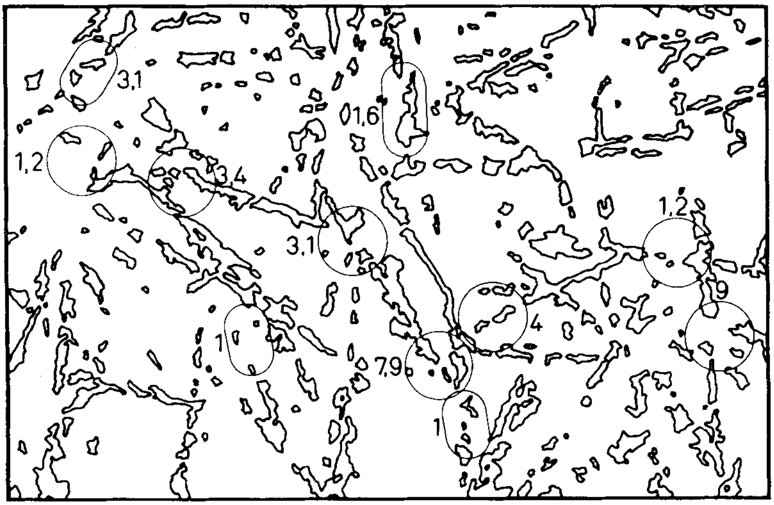

Fig. 6. Drawing of the γ_2 phase from the same area as in Fig. 5b but at a level approximately 2 μ deeper. The drawing shows the number of the levels at intervals of approximately 1 μ at which the individual γ_2 grains anastomosed. ×200.

A characteristic feature of the dissolution process was that it advanced most rapidly on the side and top surfaces of the specimens, i.e. on the surfaces most accessible to the citrate solution; there was thus no evidence of an electrochemical process of the same nature as that found with NaCl solutions with the formation of a concentration cell. No solid corrosion products were observed during the citrate tests.

In the specimens of Dispersalloy 400 the diagnosis of the γ_2 phase was less certain, and it was not therefore possible to provide absolute evidence of any dissolution. On the other hand, it was plainly seen that a reaction phase — presumably copper amalgam — which lay in the form of irregular rings on the amalgam's Ag-Cu eutectic grains was dissolved in time to an increasing depth; at the same time the citrate solution became more and more blue in color.

The mean depth of dissolution of the γ_2 phase after a particular length of time varied only slightly from brand to brand. The mean depth for all brands in each of the four aforementioned main groups was calculated for each of the five periods of time. The results are shown diagrammatically in Fig. 7 (curves A, B, C and D).

In the case of Dispersalloy 400 the depth was measured of the dissolution of the copper amalgam phase (curve E). Only a small number of specimens

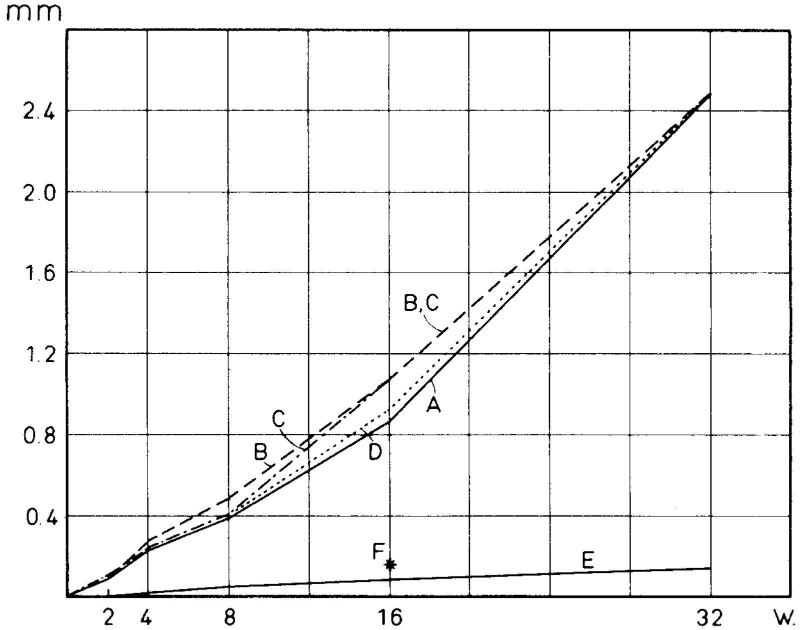

Fig. 7. The mean depth of dissolution of the γ_2 phase in relation to the time (in weeks) spent in the sodium citrate solution. A—D represent the four main groups of amalgam. E: depth of dissolution of the copper amalgam phase in Dispersalloy 400. F: depth of dissolution of the γ_2 phase in brand no. 24 (high tin content).

of brand no. 24 (high tin content) were made, and the depth of the dissolution of the γ_2 phase was measured only after 16 weeks (point F in Fig. 7).

DISCUSSION

The knowledge gradually assembled of dental silver amalgams has made it more and more clear that the corrosion properties of these materials are at least as important as their mechanical properties and precision. The studies reported in this work show that well-condensed standard amalgams possess such a structure that their γ_2 phase can be totally dissolved by corrosion. Since the volume of the γ_2 phase varies only relatively little with the mercury content of the amalgams (*Otani* & *Jørgensen*, 1967), it can scarcely be considered likely that the rather moderate variations of mercury content occurring in amalgam fillings can have a major influence on the corrosion of the fillings and on the harmful effects of the corrosion.

The volume of the γ_2 phase and thus the possibilities of this phase of forming a coherent network throughout the amalgam might be reduced considerably by employing alloys with a much lower content of tin than in the present standard amalgam alloys. It is not advisable that the tin should be replaced by copper since this would introduce another, relatively easily corroding phase in the amalgam, as is the case in Dispersalloy 400 which has a tin content of 17 % and a copper content of 12 %. On the other hand, the tin could no doubt to a great extent be replaced by silver and/or palladium (cf. German patent no. 1215865). Substitution of large quantities of tin in a standard alloy by silver is generally regarded as an adverse step, one of the reasons beeing the consequent greater rate of expansion in the amalgam during setting. This factor has not however been clarified; it is not, for example, known to what extent an appropriate distribution of particle sizes can reduce expansion, or how great expansion can be without reducing the quality of the amalgam as a restorative material.

The present study has verified in full *Brecht-Bergen* & *Loebich's* observation that porosity in an amalgam considerably accelerates corrosion of the amalgam. The explanation to this is relatively simple since porosity permits the penetration of electrolytic solutions into the amalgam, thus increasing the contact area between these solutions and the γ_2 phase; oxygen tension is probably also particularly low at the bottom of the pores. It therefore appears clear that the amalgam must be made by a technic which produces minimum porosity. Such a technic is the so-called »wet» technic (*Jørgensen*, 1967) the main characteristics of which are: (1) alloy and mercury are triturated in a ratio that produces maximum ultimate strength (*Jørgensen et al.*, 1966, Figs. 1, 2 and 3), and exess mercury is not expressed outside the cavity; (2) the amalgam is condensed carefully in the cavity, and the mercury is not removed until it forms a layer approximately 1/4 mm deep above the condensed mass. Minimum porosity in the margins of occlusal fillings is obtained by (1) overfilling the cavity, (2) burnishing the margins in excess of amalgam from the filling out over the cavity margin, and (3) by carving away the excess (*Jørgensen* & *Saito*, 1967). It should be added that a reduction in porosity has a much greater effect on the strength of the amalgam than an equally high percentage reduction of the mercury content.

SUMMARY

The corrosion of silver amalgams must be regarded as a major — possibly the principal — cause of the failure of silver amalgam fillings. This study has shown that the corrosion of dental silver amalgams depends on differences in the oxygen tension on the surface of the amalgam, and that porosity greatly accelerates corrosion. On the occurrence of corrosion, the γ_2 phase

is acted upon selectively; in all well-condensed standard amalgams this phase forms a coherent network, and consequently corrosion is not limited to the surface of the amalgam but continues until the whole γ_2 phase is destroyed.

It would presumably be possible to improve the silver amalgam's resistance to corrosion by replacing large quantities of the alloy's tin content with silver or palladium; the possibility of altering the composition of the alloy in this manner without detracting from the amalgam's other properties does not yet seem sufficiently clarified. If large quantities of the alloy's tin content are replaced by copper, the amalgam will have a considerable content of strongly corrosive copper amalgam.

Since both the corrosion and strength of the amalgam depend much more on the porosity of the amalgam than on its content of mercury, preference must be given to an amalgam technic producing the lowest possible degree of porosity (»wet» technic, burnishing of occlusal margins).

RÉSUMÉ

STRUCTURE ET CORROSION DANS LES AMALGAMES DENTAIRES

La corrosion de l'amalgame d'argent peut être considérée comme une des causes principales — peut-être même la plus importante — des échecs rencontrés avec les obturations à l'amalgame d'argent. La présente étude a montré que la corrosion des amalgames dentaires à base d'argent se produit lorsqu'il existe des différences de teneur en oxygène à la surface de l'amalgame et que la corrosion est considérablement accélérée par les porosités. Lors de la corrosion, la phase γ_2 est attaquée de manière sélective; cette phase constitue dans tous les amalgames habituels bien condensés un réseau continu, et la corrosion ne se limitera donc pas à la surface de l'amalgame, mais pourra se poursuivre jusqu'à destruction complète de la phase γ_2.

Il est probablement possible d'obtenir en ce qui concerne la corrosion une amélioration de l'amalgame d'argent en remplaçant dans l'alliage des quantités notables d'étain par de l'argent ou du palladium; la possibilité de réaliser une telle modification de la composition de l'alliage sans compromettre les autres propriétés de l'amalgame ne semble pas encore établie. Si l'on remplace par du cuivre une grande quantité de l'étain de l'alliage, on obtiendra un amalgame contenant une quantité notable d'amalgame de cuivre qui est fortement attaqué par la corrosion.

Étant donné que les porosités de l'amalgame influent nettement plus que sa teneur en mercure sur la corrosion de l'amalgame et sur sa résistance, il faudra préférer une technique de manipulation produisant le moins possible de porosités (technique «mouillée», brunissage des bords occlusaux).

ZUSAMMENFASSUNG

STRUKTUR UND KORROSION BEI DENTALEN AMALGAMEN

Die Korrosion von Silberamalgam ist als eine wesentliche, vielleicht die wesentlichste Ursache dafür anzusehen, dass Silberamalgamfüllungen versagen. Die vorliegende Untersuchung hat gezeigt, dass die Korrosion dentaler Silberamalgame Unterschiede in der Oxygentension an der Oberfläche des Amalgams voraussetzt und dass Porositäten die Korrosion wesentlich beschleunigen. Bei der Korrosion wird die γ_2-Phase selektiv angegriffen; diese bildet in allen wohlkondensierten Standardamalgamen ein zusammenhängendes Netz, weshalb sich die Korrosion nicht auf die Oberfläche des Amalgams beschränkt, sondern fortsetzen kann, bis alle γ_2-Phase destruiert ist.

Eine Verbesserung der Korrosionsverhältnisse des Silberamalgams lässt sich vermutlich dadurch erzielen, dass man bedeutende Mengen des Zinns in der Legierung durch Silber oder Palladium ersetzt; die Möglichkeiten, dass sich eine solche Änderung in der Zusammensetzung der Legierung durchführen lässt, ohne andere Eigenschaften des Amalgams zu verringern, erscheinen bisher noch ungeklärt. Werden grössere Mengen des Zinns in der Legierung durch Kupfer ersetzt, so erhält das Amalgam einen bedeutenden Gehalt an kräftig korrodierendem Kupferamalgam.

Da sowohl die Korrosion als die Stärke des Amalgams von der Porosität des Amalgams bedeutend abhängiger sind als von seinem Quecksilbergehalt, ist eine Amalgamtechnik vorzuziehen, die eine so geringe Porosität wie möglich bewirkt (»nasse» Technik, Glätten von okklusalen Kanten).

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