Progress Report

on

AN EVALUATION OF A GALLIUM–PALLADIUM–TIN ALLOY
FOR RESTORATIVE DENTISTRY
NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards1 was established by an act of Congress March 3, 1901. Today, in addition to serving as the Nation’s central measurement laboratory, the Bureau is a principal focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. To this end the Bureau conducts research and provides central national services in three broad program areas and provides central national services in a fourth. These are: (1) basic measurements and standards, (2) materials measurements and standards, (3) technological measurements and standards, and (4) transfer of technology.

The Bureau comprises the Institute for Basic Standards, the Institute for Materials Research, the Institute for Applied Technology, and the Center for Radiation Research.

THE INSTITUTE FOR BASIC STANDARDS provides the central basis within the United States of a complete and consistent system of physical measurement, coordinates that system with the measurement systems of other nations, and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation’s scientific community, industry, and commerce. The Institute consists of an Office of Standard Reference Data and a group of divisions organized by the following areas of science and engineering:


THE INSTITUTE FOR MATERIALS RESEARCH conducts materials research leading to methods, standards of measurement, and data needed by industry, commerce, educational institutions, and government. The Institute also provides advisory and research services to other government agencies. The Institute consists of an Office of Standard Reference Materials and a group of divisions organized by the following areas of materials research:


THE INSTITUTE FOR APPLIED TECHNOLOGY provides for the creation of appropriate opportunities for the use and application of technology within the Federal Government and within the civilian sector of American industry. The primary functions of the Institute may be broadly classified as programs relating to technological measurements and standards and techniques for the transfer of technology. The Institute consists of a Clearinghouse for Scientific and Technical Information,2 a Center for Computer Sciences and Technology, and a group of technical divisions and offices organized by the following fields of technology:


THE CENTER FOR RADIATION RESEARCH engages in research, measurement, and application of radiation to the solution of Bureau mission problems and the problems of other agencies and institutions. The Center for Radiation Research consists of the following divisions:


---

1 Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D. C. 20234.
2 Located at Boulder, Colorado 80302.
3 Located at 5255 Port Royal Road, Springfield, Virginia 22151.
Progress Report
on
AN EVALUATION OF A GALLIUM-PALLADIUM-TIN ALLOY
FOR RESTORATIVE DENTISTRY

by
R. M. Waterstrat*

* Research Associate from the American Dental Association in the Dental Research Section, National Bureau of Standards, Washington, D. C. 20234.

This investigation was supported in part by Research Grants DE—00949 to the American Dental Association from the National Institute of Dental Research, and is part of the dental research program conducted by the National Bureau of Standards in cooperation with the Council on Dental Research of the American Dental Association; the Army Dental Corps; the Dental Sciences Division of the School of Aerospace Medicine, USAF; and the Veterans Administration.

IMPORTANT NOTICE

Approved for public release by the Director of the National Institute of Standards and Technology (NIST) on October 9, 2015

Less accounting documents intended for use within the Government and review. For this reason, the Report has been specified that it is not available for public release.
AN EVALUATION OF A GALLIUM-PALLADIUM-TIN ALLOY FOR RESTORATIVE DENTISTRY

by

R. M. Waterstrat

1. Introduction

The use of gallium metal as a replacement for mercury in dental alloys was suggested at least as long ago as 1928, but subsequent attempts to develop satisfactory alloys for this application were unsuccessful. Further research on gallium dental alloys was conducted by the Aluminum Company of America and their studies led to the development of at least two promising alloys, one of which was patented in 1952. A systematic study of gallium alloys as possible dental restorative materials was begun at the National Bureau of Standards in 1952 and this study revealed several other alloy systems with potentially useful properties. None of these alloys have been subjected to an extensive biological and clinical investigation. They were selected primarily on the basis of their mechanical and physical properties which compared favorably with those of ordinary
dental amalgam. The present study summarizes research at the National Bureau of Standards and presents experimental data for one of the more promising gallium alloys. Much more work remains to be done, however, mainly in the biological and clinical testing of these alloys before they can be recommended for general use.

The selection of a gallium-palladium-tin alloy as offering unusual potential for use in restorative dentistry was based on an exhaustive study of many alternative binary and ternary alloys. The basis for this selection included a comparison of mechanical and physical properties together with a consideration of possible reactions with oral fluids and tissues. Alloys of nickel, for example, had been reported as possessing some outstanding physical properties; but were eliminated from consideration when it was subsequently discovered that these alloys showed a pronounced carcinogenic behavior in soft tissue implants.
2. Experimental Procedures and General Observations

A primary requirement of any gallium alloy for dental application is considered to be an ability to form a plastic mass which hardens through a diffusion reaction similar to that which occurs in dental amalgam. The convenience of using such an alloy is largely responsible for the widespread use of dental amalgam in preference to gold foil or gold alloy castings. In order to obtain hardening by such a reaction it is necessary that the alloy be capable of forming an intermetallic compound at mouth temperature. The only metals which form such compounds with gallium and have adequate resistance to corrosion in oral fluids are found within the family of transition elements or within the triad of copper, silver and gold.

Each of these metals was, therefore, mixed with liquid gallium or gallium-tin eutectic alloy (gallium + 11% tin) in order to determine which metals would harden at mouth temperature (37°C). Many of these powder-liquid mixtures would not harden at this temperature but would react rapidly with considerable
exothermic heating, if the mixtures were heated to about 400°C. In these alloys, thin oxide films may prevent the diffusion reaction at mouth temperature. The metals which formed hardenable powder-liquid mixtures at 37°C were cobalt, nickel, copper, rhodium, palladium, silver, iridium, platinum and gold. In subsequent tests of compressive strength, however, the cobalt, rhodium, iridium and silver alloys were mechanically weak and were, therefore, eliminated from further consideration. In addition, the rhodium, iridium, and platinum alloys required far too much time to complete their respective hardening reactions. Since nickel-gallium-tin alloys had been eliminated from consideration by the aforementioned carcinogenic reactions, this reduced the remaining elements to copper, palladium and gold. These three metals formed the basis for a more extensive exploration of possible gallium dental alloys. Gold-gallium alloys were eventually eliminated since they were generally not as strong as similar alloys of copper or palladium, and also because the gold-gallium alloys had an undesirable blue colored surface after hardening.
A series of tests were made using copper-gold alloy powders having compositions of 0, 35, 50, 80 and 100% Au by weight. The products of the hardening reaction in the ternary Cu-Au-Ga alloys were identified by x-ray diffraction in each case and compared with compounds reported in the binary systems Cu-Ga and Au-Ga. In each case the compounds which formed were those richest in gallium even though other binary compounds are also stable at room temperature. The relative proportion of CuGa$_2$ or AuGa$_2$ compounds which formed depended on the copper-gold ratio and there was no evidence for any mutual solubility of these compounds. The ternary alloys, however, were not appreciably stronger than the binary Cu-Ga or Au-Ga mixtures alone and were, therefore, discarded in favor of the stronger Pd-Ga alloys.

X-ray diffraction studies of hardened alloys of pure palladium powder and liquid gallium-tin eutectic alloy revealed the presence of the intermetallic compound PdGa$_5$ and some residual palladium. The compound PdGa$_5$ has a tetragonal crystal structure which is a somewhat modified version of the structure of the compound CuAl$_2$, an important hardening constituent in commercial aluminum alloys.
Fine powders of pure palladium or pure gold produce violent exothermic reactions when mixed with liquid gallium-tin alloy at room temperature. It is, therefore, necessary to dilute the pure metals with some other element before reacting the fine powder with gallium in order to reduce the amount of exothermic heating. Various elements were alloyed with palladium in a study of their effectiveness in reducing heat evolution, but in many instances the strength of the resulting alloy was lowered appreciably by the alloy addition. However, a very stable compound Pd₃Ga exists in the binary Pd-Ga alloy system and this compound will react with the liquid gallium-tin eutectic alloy without excessive exothermic heating and without reduction in strength. The alloy Pd₃Ga was prepared by arc-melting in a water-cooled copper crucible under an atmosphere of inert gas such as argon or helium. The as-cast alloy was crushed to a very fine powder; appreciably finer than is needed to pass the 325 mesh screen and having the consistency of a fine flour. This was accomplished, by grinding it in a hardened steel rod mill for several hours. A very fine particle size is essential in order to
obtain such desirable properties as high strength, optimum hardening time, moderate expansion on setting, and good surface finish in the gallium alloy mixtures. The strength increases while the setting time and setting expansion decrease as progressively finer alloy particle sizes are utilized. In mixing the Pd$_2$Ga alloy powder with the liquid gallium-tin eutectic, the proportions used were 0.09 ml of liquid per gram of powder. The liquid was dispensed from a microburet. The alloy was mixed in a Teflon$^\text{®}$ capsule without a pestle using a mechanical mixer of the type normally employed in dentistry. It was necessary to mix the alloy for about one minute when using the Wig-L-Bug$^\text{®}$ mechanical mixer. The Teflon$^\text{®}$ capsule is desirable to minimize wetting by liquid gallium. After mixing, any excess liquid may be removed with a squeeze cloth. The mixture can be handled and carved, using ordinary dental instruments. The alloy very effectively wets the tooth structure in the mouth in contrast to the behavior of ordinary dental amalgams. A typical restoration is shown in Figure 1.
3. Physical and Mechanical Properties

The compressive strength after one hour from the time of mixing averaged 23,000 psi (159 MN/m²) as compared with values of about 10,000 psi (69 MN/m²) obtained for dental amalgam under identical conditions. The gallium-palladium-tin alloy has an average fully-hardened compressive strength of about 75,000 psi (517 MN/m²) with occasional specimens showing strengths as high as 87,000 psi (600 MN/m²). This can be compared with an average value of 55,000 psi (379 MN/m²) for the fully-hardened compressive strength of dental amalgam. The tensile strengths averaged 9,700 psi (67 MN/m²) with occasional specimens as high as 12,000 psi (83 MN/m²) as compared with 8,200 psi (57 MN/m²) for dental amalgam. Thus, the gallium alloys appear to have a higher early strength than dental amalgam and a higher final compressive and tensile strength. The modulus of elasticity of the alloy, measured by ultrasonic methods, was 12.0 ± 0.6 x 10⁶ psi (83 ± 4.1 GN/m²) as compared with 9.1 ± 0.1 x 10⁶ psi (63 ± 0.7 GN/m²) for dental amalgam measured by the same method.¹⁷ These data are summarized in Table 1.

The greater strength and rigidity of the gallium-palladium-tin alloy over that of dental amalgam may be partially due to the higher peritectic decomposition temperature of PdGa₅ (200°C) as compared with that of Ag₃Hg₃.
(reported as 127°C in binary Ag-Hg alloys, but observed as about 80°C in dental amalgam). It may also be due to the virtual absence of internal voids which are a source of weakness in dental amalgams. Microscopic examination of the gallium-palladium-tin alloy reveals a dense packing of the Pd₄Ga alloy particles and remarkably few voids (Fig. 2). The Pd₄Ga alloy particles appear to be fairly uniform in size and somewhat spheroidal in shape.

The measured density of the gallium-palladium-tin alloy was 8.8 g/cm³ as compared with 11.4 g/cm³ for a dental amalgam. The thermal expansion coefficient between 25°C and 60°C of the gallium-palladium-tin alloy was 15 x 10⁻⁶ cm/cm/°C as compared with 25 to 27 x 10⁻⁶ cm/cm/°C for dental amalgam and 8 to 12 x 10⁻⁶ cm/cm/°C for tooth structure. The gallium-palladium-tin alloys had setting expansions which were usually in the range of 15 to 20 μm/cm (.15 to .20%) as compared with 0 to 15 μm/cm (0 to .15%) for dental amalgam, but the dimensional change was a sensitive function of the alloy particle size and could be readily changed.
Creep tests on the gallium-palladium-tin alloy revealed a remarkable resistance to flow under an applied load at room temperature. When loaded in tension to about half its ultimate tensile strength (4,000 psi) (27 MN/m²) the gallium-palladium-tin alloy undergoes a barely detectable flow in two weeks, whereas dental amalgam under the same conditions will flow to the point of probable fracture. The flow rate for dental amalgam was about $5 \times 10^{-5}$ inches/inch/minute while the gallium-palladium-tin alloy had a flow rate of only $7 \times 10^{-8}$ inches/inch/minute. This result may be partially explained, since room temperature, at which the test is conducted, is fairly close to the decomposition temperature of dental amalgam (80°C) whereas the gallium-palladium-tin alloy at this same testing temperature is farther from its decomposition temperature (200°C). It is likely that the higher decomposition temperature of the gallium-palladium-tin alloy will also enable it to retain its strength at moderately elevated temperatures as is the case with gallium-nickel-tin alloys.
X-ray diffraction studies reveal that the hardened alloy contains the compound PdGa₅ together with residual Pd₂Ga but there was no evidence of any other compounds. This suggests that the alloy hardens by the reaction:

\[ \text{Pd}_2\text{Ga} + 9\text{Ga} = 2\text{PdGa}_5 \]

Compounds containing tin were not detected either by x-ray diffraction or metallographic examination. The primary purpose of the tin in this alloy, however, is to lower the melting point of gallium below room temperature for convenience in mixing the alloy.

Corrosion tests on the gallium-palladium-tin alloy in distilled water at room temperature have revealed the slow formation of a gelatinous compound which ultimately crystallizes as the white gallium oxyhydroxide GaO(OH), identified by x-ray diffraction. This reaction is accompanied by a blackening of the surface of the alloy. The blackening is apparently not due to another oxide but may be caused by residual palladium or a palladium-rich intermetallic compound. The black coating was very thin and we were unable to collect enough of this material for identification. Blackening of the surface of these alloys was later observed after about one week in vital rat teeth and in vital dog teeth,
but there was no indication of any blackening or corrosion in tests in vital human teeth even when observed for two months. Conditions in the human oral cavity are difficult to reproduce in vitro and may not be satisfactorily reproduced even by the oral environment of rats or dogs. For this reason, we did not undertake any extensive in vitro corrosion testing program. Actual clinical trials would presumably resolve this question.

In view of the pronounced tendency of gallium to wet tooth structure, it appeared to be of considerable interest whether an improved marginal seal is obtained in restorations using gallium-palladium-tin alloy. An investigation of marginal leakage was conducted using the method described by Pickard and Gayford. This method entails measuring amounts of air pressure needed to produce marginal leakage in restorations in extracted human teeth. The air pressure is applied through a channel in the root canal which leads beneath the restoration. The tooth itself is immersed in distilled water during the test. Both ordinary dental amalgams and gallium-palladium-tin alloys were tested using argon gas as the pressure medium. Pressures ranging from 3 to 19 psi (2 to 13 kN/m²) were required to produce leakage
in dental amalgam restorations that had been allowed to harden for 24 hours, whereas pressures of 22 to 55 psi (15 to 38 kN/m²) were required to produce leakage in 24-hour restorations of the gallium-palladium-tin alloy. The amalgam restorations after five weeks required pressures varying from 69 psi (48 kN/m²) to over 100 psi (69 kN/m²). No attempt was made to apply pressures greater than 100 psi due to possible explosion hazards. After 48 hours, all of the gallium-palladium-tin restorations were leak-tight at pressures of over 100 psi and they all remained leak-tight when retested after four weeks. All of the restorations were made by the same operator using, as far as possible, identical techniques. The gallium-palladium-tin alloy, therefore, seems capable of consistently producing a more effective seal at the margins of a restoration than is usually obtained with ordinary dental amalgam.

The gallium-palladium-tin alloy, when contaminated with a 0.6% saline solution, did not undergo a "delayed expansion", but did have a greatly increased initial setting expansion of up to 420 μm/cm (4.2%). Therefore, the gallium-palladium-tin alloy, like zinc-containing amalgam, should not be contaminated with moisture during mixing or packing.
4. Clinical and Biological Studies

Tests for tissue tolerance and corrosion resistance are, of course, essential and some preliminary tests were conducted in various laboratories. The copper-gallium alloys were evaluated initially by means of subdermal implants in guinea pigs and were found to produce a rather severe reaction. Similar severe reactions to subdermal implants of gold-gallium alloys and palladium-gallium alloys were observed in rats. However, in contrast to the nickel-gallium alloys, no carcinomas were detected.

These findings, however, may be somewhat irrelevant since the alloys are intended for use as restorations of lost tooth tissues and not as subdermal implants in soft tissues. Studies of pulp reactions may provide a more appropriate basis upon which to evaluate the performance of the gallium alloy as a dental restorative material. At the same time one can obtain information on the corrosion resistance of the material in an oral environment. Preliminary studies were begun using vital teeth in both rats and dogs. In each case the surface of the gallium alloy restorations turned black within one week after being placed, and it appeared that a further study of the corrosion of these alloys
was needed. Since laboratory corrosion tests were unreliable in evaluating the performance of this material, it was suggested that the corrosion tests might be performed in an actual oral environment using caries-free human vital teeth that were eventually to be extracted in preparation for full dentures. Additional information on pulp reactions could also be obtained on the extracted teeth. These studies were begun in 1963 by Dr. H. Swerdlow and Dr. H. R. Stanley at the National Institute of Dental Research using the gallium-palladium-tin alloy.

In a preliminary study 20 fillings were placed in 5 patients for periods of time ranging from 1 day to 84 days, followed by extraction and histopathological examination. There was no evidence of any corrosion and the pulp reactions were similar to those normally obtained with conventional dental amalgam, which usually presents a small percentage (less than 5%) of severe lesions. It seemed rather surprising that the test results for corrosion using rats and dogs were not in agreement with the tests in humans. Some of the gallium-palladium-tin alloy used by Drs. Swerdlow and Stanley was submitted to Drs. L. and K. Langeland at the State University of New York at Buffalo who subsequently reported
severe pulp reactions to this alloy in vital monkey teeth. Much more data are needed to evaluate adequately the biological behavior of this alloy.

We have recently learned that some of the gallium-copper-tin alloys that were developed during the early stages of this research have been subjected to clinical tests with favorable results. Nevertheless, the use of gallium-copper alloys may be premature. Even though copper amalgams have been used in dentistry for many years, there has been little work done on possible pulp reactions or toxicity and their corrosion resistance is marginal. On the other hand, palladium is normally quite inert at mouth temperature, and both palladium and gallium are reported to have low toxicities.

5. Conclusion

Gallium-palladium-tin alloys possess many of the properties desired in a dental restorative material. When compared with dental amalgam the gallium-palladium-tin alloys exhibit superior strength and vastly superior resistance to flow under an applied load at mouth temperature. The gallium-palladium-tin alloys also possess thermal expansion coefficients that more closely match those of human teeth.
The gallium alloys effectively wet the tooth structure and this apparently produces a tighter marginal seal than is usually obtained with dental amalgam.

It is concluded that the use of a gallium-palladium-tin alloy offers several significant advantages over dental amalgam as a restorative material and that this alloy possesses some outstanding physical and chemical properties. Its use in clinical dentistry, however, must await a much more extensive study of its biological properties.
References


<table>
<thead>
<tr>
<th>Physical Property</th>
<th>Dental Amalgam</th>
<th>Gallium-Palladium-tin Alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Compressive Strength*</td>
<td>55,000 psi (379 MN/m²)</td>
<td>75,000 psi (517 MN/m²)</td>
</tr>
<tr>
<td>Average Tensile Strength*</td>
<td>8,200 psi (57 MN/m²)</td>
<td>9,700 psi (67 MN/m²)</td>
</tr>
<tr>
<td>Modulus of Elasticity</td>
<td>9,100,000 psi (63 GN/m²)</td>
<td>12,000,000 psi (83 GN/m²)</td>
</tr>
<tr>
<td>Compressive Strength* 1 hr from time of mixing</td>
<td>10,000 psi (69 MN/m²)</td>
<td>23,000 psi (159 MN/m²)</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion between 25°C and 60°C</td>
<td>$25 \times 10^{-6}$ CM/CM/°C</td>
<td>$15 \times 10^{-6}$ CM/CM/°C</td>
</tr>
<tr>
<td>Creep or Flow Rate at room temperature under a load of 4,000 psi</td>
<td>$5 \times 10^{-5}$ in./in./min.</td>
<td>$7 \times 10^{-8}$ in./in./min.</td>
</tr>
</tbody>
</table>
Legend of Figures

Figure 1. Gallium-palladium-tin alloy restorations in human vital teeth.

Figure 2. Photomicrograph of a fully hardened gallium-palladium-tin alloy. Particles of the alloy Pd$_2$Ga embedded in a matrix of PdGa$_5$ compound.

Magnification 1200x
Original Magnification 500x