AN INVESTIGATION OF THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF ELECTROCHEMICALLY COATED Ag_4Sn DENTAL ALLOY PARTICLES CONDENSED IN VITRO

by

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DEDICATION

I dedicate this dissertation document to my mother Daisy Marquez. When my father Juan Marquez was tragically killed in an automobile accident in 1948, leaving behind four orphaned boys, I was 9 years of age and the oldest of the Marquez brood. Since she spoke Spanish only, and had no formal education or vocational skills, she leaned on me to help her through the crisis. She and I formed a close relationship to carry on the struggle for survival without my dad.

I would interpret for her, assist her in filling out forms, and advise her on all matters having to do with paperwork. To help with money, I worked after school shining shoes and would help her pick cotton and onions on weekends. Between the two of us, and subsequently with the help of my younger siblings as they came of age, we eked out a living in the rural communities of San Elizario and Ysleta. It was difficult, and sometimes we did not eat well, but we were united as a family and went to church often to pray for guidance.

Mother and I would discipline my three younger brothers as a team, much like husbands and wives do in normal families. She admonished me to do well in school so that I could set a good example for my siblings and be able to escape the drudgery of the agricultural jobs that we worked. And she would always provide my brothers and me with plenty of love and affection.

Our bond remained very strong, even when I was in the Navy or away to

college. This strong family unity convinced me to change professions while working as an engineer in the Houston area, so that I could return to El Paso to be close to her and my brothers. She was the magnet that drew me back.

Presently, she is 80 years old, healthy and going strong, and still revered as the matriarch of the Marquez family. I will always admire her for being the stern maternal figure who kept the family together during trying times, and for loving us and teaching us how to love. It is for these reasons and for so many others that I sincerely and humbly dedicate this dissertation document to my mother as but a small token of my gratitude for all that she has done for me.

Gracias, madre, por darme la vida y la inspiración para educarme. La sigo queriendo con todo mi corazón y siempre le deseo salud y felicidad. Que Dios la bendiga y la güarde muchos, muchos años.

Su hijo fiel,

Tony

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ACKNOWLEDGEMENTS

Were it not for the thoughtful and considerate advice that my mentor, Dr. Lawrence E. Murr, provided for me throughout the academic challenges that I faced in the UTEP classrooms and laboratories while seeking to obtain the Ph.D. in materials science and engineering, I can undeniably state that I would not have succeeded in this endeavor. His door was always open for me, whether to counsel me on homework assignments, research papers, and laboratory procedures, or simply to provide a sympathetic ear to any personal problems that I sought to share. The social gatherings at his house, where opinions and scientific information were exchanged and shared with fellow students and faculty, were very important and much appreciated. He and his wife Pat were always gracious hosts.

I also would like to gratefully acknowledge Miss Viviana Agüero, undergraduate student in metallurgical and materials engineering, for her able and enthusiastic laboratory assistance. She was absolutely invaluable in helping me prepare specimens for characterization with optical and scanning electron microscopy, in transferring digital images to color film, in obtaining x-ray diffraction patterns, and in getting microhardness readings. Whenever I needed her to do an experiment or run an errand for me, she was cheerfully obliging. More than that, she was my buddy, always ready to listen to my concerns.

Dr. Elizabeth Trillo, with whom I shared office space in the specimen preparation laboratory, is also hereby sincerely acknowledged. Although many years my junior, she provided me with wise advice on the operation of laboratory equipment for my experiments and also on the preparation of my dissertation document. She always made me feel welcome in the laboratory. The jigs for compression testing experiments were kindly manufactured by our skillful departmental technician, Mr. David Brown. He was always concerned for the safety and success of the students in the department, and displayed a cheerful disposition whenever I asked him to help me resolve technical problems during the research.

The other members of my faculty advisory committee should also be thanked: Dr. Roy Arrowood for his patient and gentle demeanor in explaining so many technical things to me, Dr. Russell Chianelli for his expert technical advice on specific chemical topics and for helping me procure the fluoroboric acid to acid-wash my specimens, and Dr. Dwight Russell for his sincere enthusiasm and kind compliments regarding my research.

I especially wish to thank Dr. David Lashmore, Research Director of Materials Innovation, Inc. in West Lebanon, New Hampshire, for graciously providing me and UTEP with the materials necessary to carry out this investigation. He was the intellectual spark that ignited my interest in embracing this project after I listened to his UTEP lecture in the spring of 1994 on the new,

patented silver-coated intermetallic particles that he helped develop at the National Institute of Standards and Technology. Since my scientific investigation was not funded, his periodic shipping of the coated materials and his expert technical advice throughout the project were absolutely essential for its realization. I thank him very sincerely.

I also wish to thank Dr. Lashmore for warmly welcoming my brother Richard and me when we went to visit his facility in New Hampshire in the spring of 1997. We had driven through a blinding blizzard from Boston to West Lebanon and he was there to greet us, feed us, and arrange for free motel accommodations. We could not have asked for a better host under such stressful and trying circumstances!

Mr. Guy Crawford, Ph.D. student in materials science and engineering, guided Viviana and the author in obtaining numerous ESEM images and EDS element density maps and plots in the chemistry department. His kind assistance is sincerely acknowledged.

Last but not least, I would like to express my appreciation to my faithful and devoted dental staff. My time away from the office to participate in this Ph.D. program many times caused inconveniences and hardships for them. I thank them for their understanding, support, and patient indulgence.

ABSTRACT

Dental amalgams, popularly known as silver fillings, have been the posterior restorative material of choice by dentists in the U.S. for more than 160 years. Through the 1970's, over 75% of all directly-placed posterior restorations in the mouths of the American population were dental amalgams. In the last 20 years, however, the use of amalgam restorations has been declining due to decreased incidence of caries, availability of more tooth-colored restorative materials, and reluctance of some patients and dentists to use them. In 1991, silver amalgam accounted for about 50% of all restorations [1].

Amalgam's main alloying constituent is mercury, an element usually associated with toxicity to the human organism. Mercury dissolves and fuses the other metallic components of Ag, Sn, and Cu in the dental alloy powder mixture into a workable plastic mass that is condensed by the dentist into a prepared tooth cavity. After setting, amalgam becomes a stiff and brittle metal-matrix composite with good compressive strength, poor tensile strength, good creep properties (in high-copper alloys), and adequate corrosion resistance to withstand the harsh electrochemical conditions of the oral environment.

The mercury in the mixture, approximately 50 wt.%, reacts with the alloy powders to precipitate new intermetallic phases during the amalgamation reactions, and becomes chemically bonded to its surrounding structures. After

the restoration sets and hardens, mercury is no longer available to react with the oral environment, except in very minute amounts. Numerous efforts to replace amalgam have been unsuccessful because no posterior restorative biomaterial has been developed that has its ease of manipulation, compressive strength, biocompatibility, wear and corrosion resistance, and inexpensiveness.

As part of the ongoing scientific effort to develop a new amalgam-like material without mercury, a team of metallurgists and electrochemists at the National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland, announced in 1993 the development of a new Ag-Sn dental alloy system without mercury that sought to replace conventional dental amalgams. They used spherical Ag_3Sn *and* Ag_4Sn *intermetallic dental alloy particles, commonly used in conventional dental alloys, and coated them with electrodeposited silver with newly-developed electrolytic and immersion techniques. The particles had relatively pure silver coatings that were closely adherent to the intermetallic cores.*

These silver-coated particles, due to silver's plasticity at room temperature, were condensed into Plexiglas® molds with the aid of an acidic surface activating solution (HBF_4*) and a mechanical condensing device, producing a metal-matrix composite with* $Ag_{3,4}Sn$ *filler particles surrounded by a cold-welded silver matrix. Since silver strain hardens rather easily, the layers had to be condensed in less than 0.5 mm increments to obtain a dense*

structure. Mechanical testing at NIST produced compressive strength values equal to or greater than those of conventional dental amalgams.

Because of its potential for eliminating mercury as a constituent in dental amalgam, this material created a stir in dental circles when first developed and conceivably could prove to be a major breakthrough in the field of dental restoratives. To date, the chief impediments to its approval for human clinical applications by the Food and Drug Administration are the potentially-toxic surface activating solution used for oxide reduction, and the high condensation pressures needed for cold welding because of the tendency for silver to strain harden.

In this related study, the author, who has practiced general dentistry for 25 years, evaluates some of the mechanical and microstructural properties of these electrochemically coated particles when they are amalgamated with mercury. Because of patent restrictions for the coated particles that protect the cold-welding work being done at NIST, these particles necessarily had to include mercury as a constituent for this investigation. No other industrial or academic laboratory, however, has ever investigated the microstructural and mechanical properties of these coated particles when mixed with mercury, making this study rather unique.

This investigation was conducted in the laboratories of the Departments of Chemistry, Geological Sciences, Metallurgical and Materials Engineering (MME),

and at the Materials Research Institute (MRI) of the University of Texas at El Paso, El Paso, Texas. Dr. L.E. Murr, my mentor, provided the inspiration and technical advice. Miss Viviana Agüero, an undergraduate student in MME who was assigned to collaborate in this project, assisted with laboratory experiments through the entire study. The compressive testing jigs were machined and assembled by Mr. David Brown, support technician in MME.

The electrochemically coated Ag_4Sn intermetallic particles, both with silver and copper coatings, were provided to UTEP free of charge by Dr. David Lashmore, Research Director of Materials Innovation, Inc., West Lebanon, New Hampshire, and formerly a member of the scientific team that developed the coated particles at NIST. Specific processes used in the coating techniques are proprietary and licensed under U.S. patent 5,603,815 issued 2/18/97 to Dr. Lashmore, et.al., and the American Dental Association Health Foundation.

The as-received particles were characterized for general morphology, surface features, crystallography, and size distribution with x-ray diffraction (XRD), optical microscopy (OM), and scanning electron microscopy (SEM). Amalgamated specimens were tested to failure in standard compression jigs fabricated according to ADA Specification #1, and also for surface hardness with a Vickers microhardness indentor. The microstructural and chemical features at the interfaces, interphases, and fracture surfaces were studied with OM, SEM,

and energy-dispersive x-ray spectroscopy (EDAX). Values obtained were compared to baseline data from measured mechanical and microstructural properties of Tytin®, a high-copper, single composition, ternary phase alloy that was used as the control in this study. The author has used Tytin regularly since 1980 as his restorative material of choice for posterior teeth.

Since the author approached this materials science investigation with a background as a dental clinician, this dissertation document includes as an introduction: (1) a general review of the anatomy, biology, and electrochemistry of the oral cavity, (2) a description of the process of mastication, (3) a brief outline of the chemical and mechanical properties of conventional dental amalgams, (4) a cursory look at the chemistry and toxicity of mercury, and (5) a comparison of the clinical characteristics and mechanical properties of some newly developed amalgam-like materials, including gallium alloys and the cold-welded Ag-coated particles that Dr. David Lashmore and his associates developed at NIST.

The concluding portion of this document reviews and discusses results of the UTEP laboratory experiments and offers suggestions for future procedures to improve the system. Regrettably, this three-year investigation has determined that mercury is unable to completely wet these electrochemically coated particles at room temperature, whether their coatings are silver, copper, or mixed, and/or whether Cu and Sn metallic powders are added. This lack of chemical reaction

with mercury is because naturally occurring oxide coatings reduce the surface energy of the particles by satisfying unfulfilled bond sites. These oxides, which affected the smoothness and integrity of the Ag coated surfaces, as well as the chemical bond at the particle-coating interface, produced voids and pores on the coatings, and were responsible for the separation and peeling of some coatings.

They also prevented matrix phases that are typically formed through conventional amalgamation reactions from having contiguous physical and chemical contact with the coated surfaces. The lone exceptions were the 18% Ag-coated particles with dendritic surface structures that permitted mechanical interlocking at the gamma-1 matrix/dendrite interface and had the strongest compressive strengths. Other specimens without the dendrite coatings demonstrated an interruption in continuity across interfaces and interphases, resulting in weak compressive strengths (10-40% of control), and their fracture surfaces exhibited ductile failure characteristics in the matrix and a more brittle separation at the particle-matrix interface.

Several efforts were made to remove the oxides by annealing under argon and/or by acid washing with dilute acetic and fluoroboric acid solutions. Since thermodynamic conditions were highly favorable, however, for formation of copper and silver oxides (as well as some silver sulfides) at room temperature, the particle surfaces reoxidized almost immediately and subsequently were

unable to react completely with mercury. This reoxidation occurs in other coated biomaterial systems, as was corroborated in part from conversations with materials scientists at the Surfaces in Biomaterials Symposium, Tucson, Arizona, in September 1998 and the International Association for Dental Research Conference, Vancouver, Canada, in March 1999.

The principal conclusion reached from investigating this coated-particle alloy system is that it has no potential for commercial applications in clinical dentistry due to the tenacity of the oxide coatings, and also because of the relatively large sizes of the particles. Coated particles ranged in diameters from about 50 to 250 microns, as compared to 15 to 60 microns diameters of atomized spherical particles in commercial alloys. All other things being equal, since smaller particles have more surface area per unit volume than larger particles, mercury can wet a small-particle system better. But since the coating process has minimum size limitations that prevent it from producing particles smaller than about 50 microns, smaller particles were not contained in the batches shipped.

Another practical impediment to the success of this metallic alloy system is that dentistry in the United States is inexorably moving towards other materials, such as glass ionomers, composite resins, and ceramics, that are tooth-colored and more esthetically pleasing than amalgams. Even though

these alternative materials have poor wear resistance, low packing efficiency, and susceptibility to dissolution in saliva, they are still in high demand for their esthetic value. Since they are more expensive and technique-sensitive than amalgam, their popularity likely will be confined to dental clinics in the United States, Canada, Scandinavia, and western European countries - primarily in modern, sophisticated societies where people can afford to be selective.

Because of their durability, ease of manipulation, and inexpensiveness, however, amalgams will continue to be the workhorse of dental materials, especially in third-world developing countries. And materials scientists likely will continue their quest to replace the system, or incrementally improve it. Amalgams have endured over 160 years of faithful dental service in the United States without causing any documented ailment to the human organism, and will likely remain the dental restorative material of choice despite occasional grumblings about the presence of mercury in its formulation.

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