6-1985

Corrosion of Orthodontic Brackets: Cost, Cold Worked, and Powdered Metal

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Abstract

Corrosion Resistance of Orthodontic Brackets:
Cast, Cold Worked, and Powdered Metal

by

Timothy C. Ballweber, DDS.

The purpose of this study is to evaluate the relative corrosion rates of 316-L stainless steel cast metal, cold worked, and powdered metal brackets. This is done using potentiodynamic anodic polarization to measure the voltage difference between the samples and a reference electrode. Corrosion layers effect current flow and by plotting how the current responds to an applied voltage it is possible to determine the corrosion rate of a sample. The point at where the applied voltage breaks down the passivation or oxidation layer is recorded and the relative corrosion rate is figured using the formula: Corrosion Rate$_{(mpy)}$(in milli inches per year)=[(K)(I_{corr})Equivilant Weight]/Density.(K is a known constant and I_{corr} is current density in microamps per cm^2) The results indicate that the powdered metal samples had the smallest relative corrosion rate with $.2256_{mpy}$, cast metal was next with $.4639_{mpy}$, and cold worked had the greatest corrosion rate with 2.8135_{mpy}.

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CORROSION OF ORTHODONTIC BRACKETS:
Cast, Cold Worked, and Powdered Metal

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A Thesis in Partial Fulfillment of the
Requirements for the Degree of Master of Science
in Orthodontics

June 1985

Each person whose signature appears below certifies that this thesis in his opinion is adequate, in scope and quality, as a thesis for the degree Master of Science.

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ACKNOWLEDGEMENTS

The author wishes to express his appreciation to the following individuals who assisted in the development of this paper:

Drs. Garland Scott, Milford Anholm, Virgil Heinrich, and Willis Schlenker for serving on my research committee.

Dr. E. Pye of the corrosion research lab at California State Polytechnic University, Pomona, for use of his equipment in this project.

Mr. Jim Stevenson, graduate student in corrosion research at California Polytechnic University, Pomona, for his time and expertise in helping me set up the experimental techniques and running the corrosion tests essential for this project.

Mr. Dale Carriere of the Electron Microscopy Center, California State Polytechnic University, Pomona for running the scanning electron microscope.

Special acknowledgements are extended to Dr. Garland E. Scott for his original idea for this project and his help and patience throughout.

The Foundation for Orthodontic Research for supporting and funding this project.

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CHAPTER 1

Introduction

Orthodontic brackets fabricated from powdered metals will be made available to the orthodontic profession in the near future. Powdered metals technology is presently in limited use in orthodontics as a coating for bonding bases to increase mechanical retention.[1] Parts manufactured from powdered metallurgy has been available for some time for use in industry and aviation, but techniques producing close tolerance products, such as brackets, have been unavailable. Recently a new technique, "injection molding", of these powdered metals has been developed.[2,3] This is similar to the process by which plastics are manufactured and allows for the fabrication of smaller and more precise metal parts. Experts in the orthodontic materials industry have become interested in this method as it provides a more convenient, inexpensive, and quality controlled product.

Presently there are three methods for fabricating brackets: cast metal, cold worked or machined(wrought), and the new powdered metal technique. All three are fabrication techniques which will produce stainless steel parts. There are several instances in the literature documenting corrosion of stainless steel brackets but no known work has been done comparing the relative corrosion rates of the stainless steel parts produced from these different processes.

With the introduction of powdered metals it is important to establish a standard of comparison as to which process provides the greatest corrosion resistance. It is the purpose of this paper to evaluate the relative corrosion rates of orthodontic brackets produced from the three fabrication processes.

CHAPTER 2

Review of the Literature

In recent literature there has been observation made of stains on teeth thought to be associated with corrosion of resin-bonded stainless steel brackets.[4] Gwinett found that 60 percent of respondents in a survey noted staining of bonded appliances and 25 percent reported stains present on the teeth after the bonding material was removed.[5] This observation was also made by Maijer who concluded that use of stainless steels of improved corrosion resistance would overcome this problem.[6]

In dentistry there is considerable research being done to evaluate the corrosion of base metal alloys but little if any research being done looking at the corrosion resistance of the various stainless steels used in orthodontics.[7] Interest in corrosion resistance of orthodontic brackets is increasing with enamel staining being seen and also with the increased use of some of the new bracket recycling methods. Buchman evaluated the effects of recycling orthodontic brackets and concluded that some methods create carbide separation in the metal and in turn create changes in the metallurgical microstructure.[8] It was suggested that these changes in a cast bracket makes it more prone to corrosion.[9] On the other, methods utilizing heat may lead to stress relief or softening of cold worked metals along with a increase in its corrosion resistance.[10] There is also considerable interest in pitting or crevice corrosion and its contribution to discoloration of teeth. Orthodontic brackets in their inherit design of tubes and slots are especially susceptible to crevice corrosion. The crevices or pits can lead to sites of significant metal destruction.[11]

The majority of research evaluating relative corrosion rates of stainless steels is being done in industrial or biomedical research.[12] Amaya conducted corrosion tests of industrial powdered metals parts using potentiodynamic polarization.[13] Sutow,et al, used the same test to evaluate corrosion resistance of the 316-L stainless steel (both cold worked and cast) used for orthopedic implantation.[14] While the results of their research are valuable, there are no known corrosion studies of orthodontic brackets published which use potentiodynamic polarization as a basis for comparison. Such a study would give some objective guidelines for evaluating corrosion in the oral environment.

CHAPTER 3

Methods and Materials

Corrosion specimens were prepared from type 316-L stainless steel orthodontic brackets(supplied by Unitek Corporation, Monrovia, Ca.). These were divided into three groups: powdered metal, cast metal, and machined metal. Electrodes were attached to these brackets using Chomeric 10-30 vinyl cement(see appendix-1). This is a silver-plated, copper filled silicone based vinyl. These were then mounted in acrylic with one surface exposed. The exposed surface was polished to a #600 grit finish and isolated with lacquered enamel.

Measurements were made using a model 173/376 potentiostat/galvinostat(see appendix-2) and a standard Calmel electrode for a reference electrode. Voltages were recorded with a Universal Programer model 175(see appendix-2). The experimental technique consisted of immersing the samples in an electrolyte (aerated normal saline) and reading the voltage difference between the metal and the reference electrode. This experiment was run at a 5mv per second sweep with a range of -300mv to +400 from resting potential.

Five samples of each type were run according to the standard reference method[15] and standard potentiodynamic anodic polarization plots were made. All polarization plots were similar with the one being best representative from each sample group used to determine the relative corrosion rate. Samples of the powdered metal were then run again interrupting the sweep and removing the samples at various points on the plot. These points were at passivation, general corrosion, and pitting corrosion. These samples were examined in an AMR-1000 scanning electron microscope(see appendix-3) at x1000 and x10000 using positive imaging and deflection modulation. Observations were recorded using Polaroid type 52 film.

The relative corrosion rate[16] of each sample was determined by using the formula $CR_{(mpy)}=[(K \times I_{corr})EW]/D$, whereas:

$CR_{(mpy)}$= the corrosion rate in milli inches per year.
K= known constant, .013
I_{corr} = the corrosion current density in microamps per cm^2.
EW= equivalent weight which is the molecular weight divided by the number of electrons given off. EW is 27.9gms.
D= density of the metal in gms per cm^3 which is equal to 7.86.

The current density, which in this study, was recorded from the point at which the passivation layer breaks down, was also recorded. A low current density indicates a lower tendecy to corrode than does a higher one.

Pitting corrosion was evaluated from the standard plots. The area of the plot (figure 1.) between C and D is where pitting corrosion is thought to occur. That plot with the smallest or "shortest" area between these two points would then have a greater resistance to pitting or crevice corrosion.

CHAPTER 4

Results

The relative corrosion rate of each sample is given in table 1. This is given as the corrosion rate in milli inches per year[$CR_{(mpy)}$] with the sample which has the lowest $CR_{(mpy)}$ being the least corrosive.

Powdered Metal	Cast Metal	Machined Metal
$.2256_{(mpy)}$	$.4369_{(mpy)}$	$2.8135_{(mpy)}$

(table 1-- Relative corrosion rates of sample materials given in milli inches per year.)

The current densities are recorded in table 2. This is given as microamps of current at which the passivation layer is broken down and general corrosion occcurs. The sample with the lowest current density has a lower tendency to corrode.

Powdered Metal	Cast Metal	Machined Metal
.11 microamps	.25 micro amps	1 microamp

(table 2--Current densities of sample materials given in microamps.)

The potentiodynamic polarization plots (Figs. 2,3,&4) show which samples have greater propensities toward pitting corrosion. The area of the plot between C and D (Fig. 1) is where pitting corrosion is thought to occur. That plot with the smallest or "shortest" area between these two points would then have a greater resistance to pitting or crevice corrosion. Figures 2,3,&4 show that the cast metal sample has a greater resistance to pitting corrosion with the cold worked samples showing the least resistance.

The samples were examined with scanning electron microscopy at x1000 and x10000 using positive imaging and deflection modulation. This was done to evaluate the samples for any unusual surface reactions. Nothing out of the ordinary was observed. Powdered metal brackets are thought to have a greater pitting potential from incomplete closure of open surface pores.[13] An example of an "open surface pore" is shown in figure 5.

CHAPTER 5

Discussion

Most corrosion phenomena are explained in terms of electrohemical reactions.[15] It would then seem practical that one could use electrochemical techniques to study corrosion. Current-potential relations which are measured under controlled conditions can generate infromation on corrosion rates, coatings, passivity, pitting tendencies, and other data. Potentiodynamic anodic polarization is the characterization of a metal specimen by its current potential relationship. The sample is forced to act as an anode such that it corrodes or forms an oxide layer. This is the basis for the electrochemical corrosion theory. When a metal is immersed in a corrosive environment there is both reduction and oxidation reactions occuring, e.g., the metal corrodes or oxidizes and the medium is reduced. The corrosion potential is measured by determining the voltage difference between the metal specimen and an appropriate reference electrode. In this study we used a saturated calmel electrode (Hg/HgCl) which has a known voltage as opposed to the sample voltage which is unknown. A plot is made of current response as a function of the applied potential or voltage. This plot is termed a potentiodynamic polarization chart. These corrosion characteristics can then be measured and compared. A complete current-potential plot can be measured in a few minutes. Figure 1. shows an example of a plot illustrating its various components.

Stainless steel is an austenitic alloy in which iron, chromium, and nickel are in a solid solution. It is generally thought that the Ni and Cr form monolithic oxide layers on the surface to give stainless steel its good corrosion resistance. Orthodontic brackets are normally made from American Iron and Steel Institute (AISI) type 303, 304, 304L, and 316L stainless steel. As the AISI type number increases the carbon content decreases.(see table 3)

	Composition in %						
Grade	Cr	Ni	Si	Mo	Mn	S	C
303.....	18.0	9.0	1.0	...	0.2	.15	.15
304.....	19.0	9.0	1.0	0.6	0.2	.03	.08
304L....	18.5	10.5	0.7	...	0.25	...	.02
316L....	17.0	13.0	0.7	2.5	0.2	...	.02

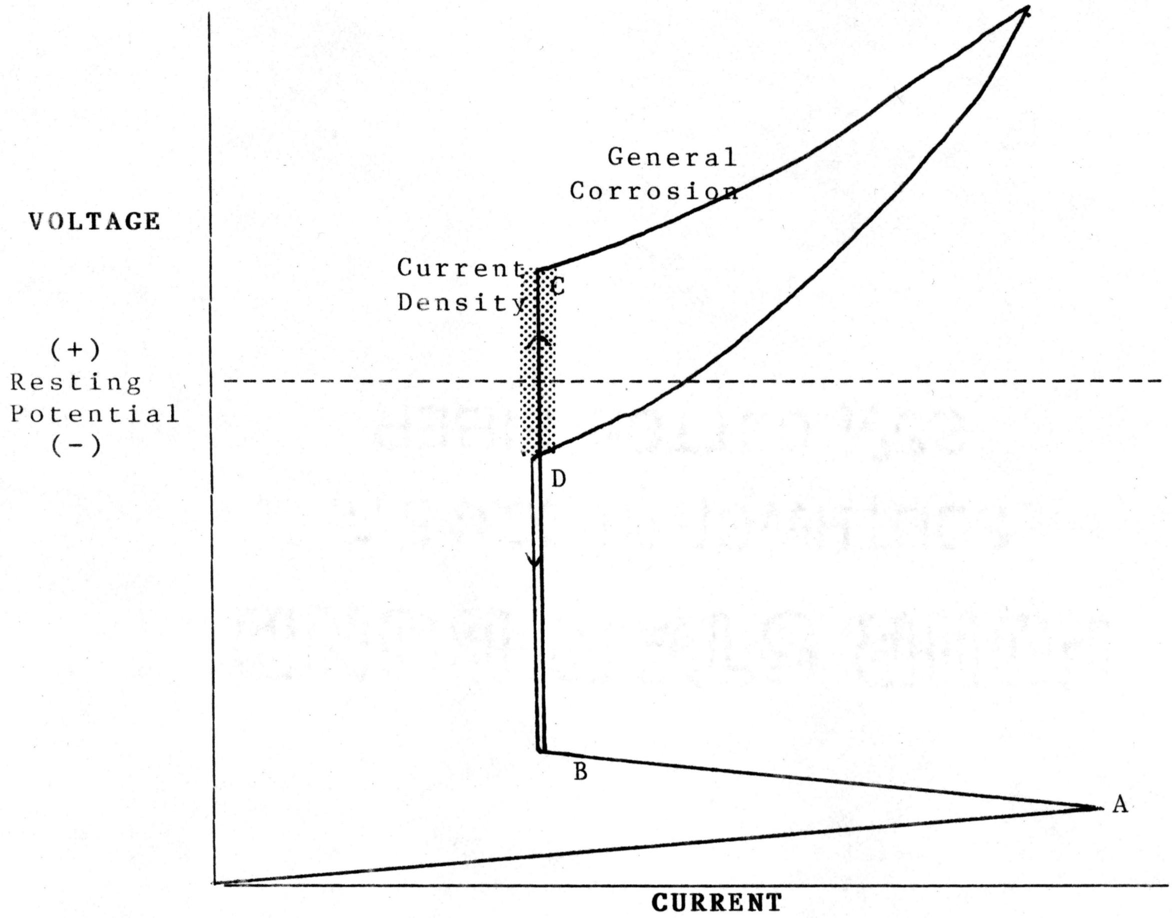
(Table 3.--Nominal compositions of stainless steel[18])

The stainless steels with a lower carbon content give up some in hardness and strength but have superior corrosion resistance or passivating properties which makes them less susceptible to corrosion. Most orthodontic brackets are made from type 304 which is a high carbon stainless steel. A low carbon AISI type 316L stainless steel is used in the making of powdered metal brackets. Maijer[6] reported no staining with type 316L, just with 304 stainless steel.

There are other elements added to 316L stainless steel to improve specific properties including molybdenum which enhances corrosion resistance, paricularily to pitting.[5] Research also indicates that resistance to corrosion is a strong function of the content of sulphides, particularily Manganese-Sulphide, which are not found in the powdered metal brackets but are found in the cast and machined samples.[13] It is impossible to remove the Manganese from the cast and wrought materials as it is inherit in most casting process. The powdered metal is Manganese free due to the purity of raw materials and the injection molding process.

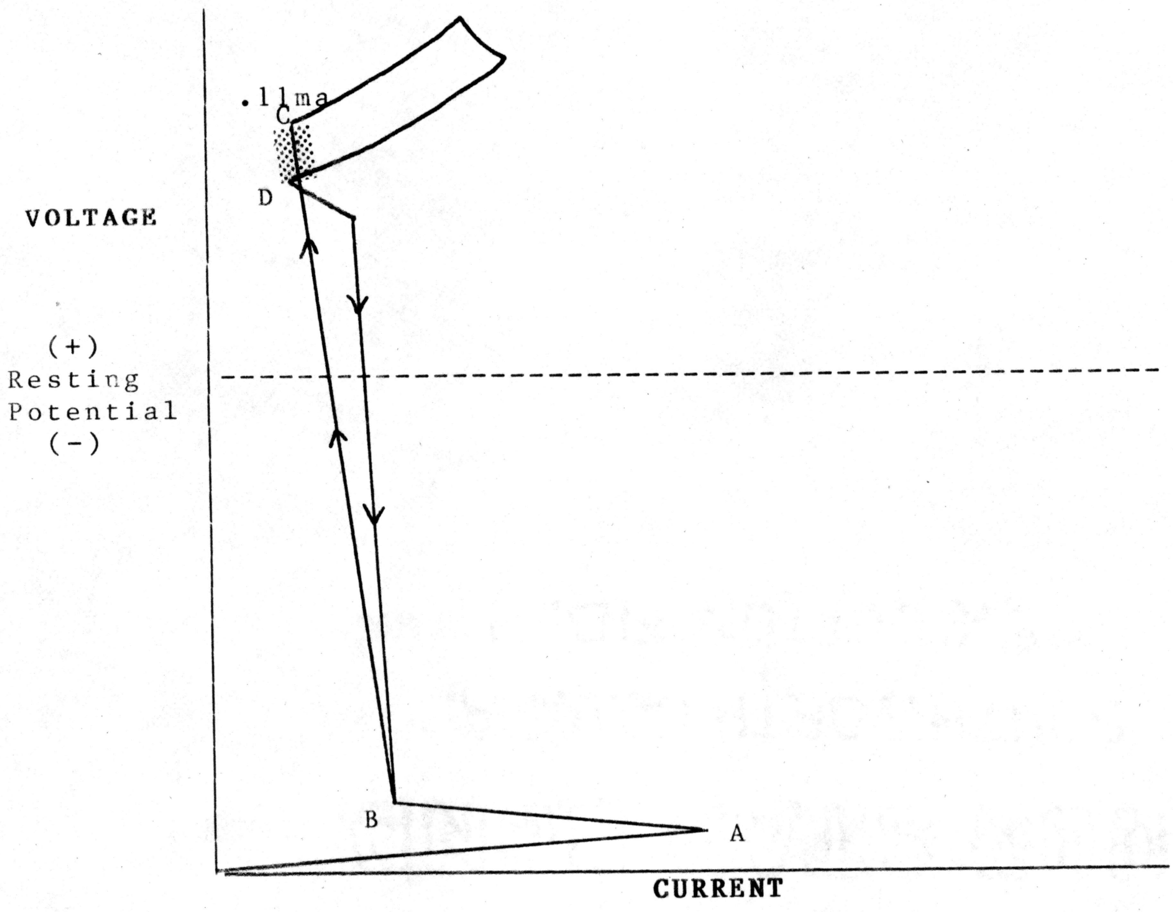
The results taken from the polarization plots and calculated for $CR_{(mpy)}$, indicate that the powdered metal stainless steels have a lower relative corrosion rate than the cast and the machined. The machined or cold worked metals show a considerably higher relative corrosion rate compared to either the cast or powdered metal. This can be associated to much of what was discussed previousily. The polarization plots (Figs. 2,3,&4) show that the powdered metals passivation breaks down at a lower current than the cold worked or the cast, which has been suggested to indicate a greater resistance to corrosion.[16] This is theorized in that two samples may be at equal voltage levels, the sample which allows the higher current flow loses its passivation layer much sooner and has less resistance to corrosion. This is illustrated in figures 2,3,&4. These are representative of the original polarization plots.

These plots also show which samples have greater propencities toward pitting corrosion. The area of the plot between C and D (Fig. 1) is where pitting corrosion is thought to occur. That plot with the smallest or "shortest" area between these two points would then have a greater resistance to pitting or crevice corrosion. Figures 2,3,&4 show that the cast metal sample has the greater resistance to pitting corrosion with the cold worked samples showing the least resisitance. It is thought that the powdered metal brackets, which are injection molded as metal spheres and then sintered,[17] may have a greater potential towards pitting corrosion from incomplete closure of open surface pores (Fig. 5) and with the polishing action[13] of the experimental technique. This study did not indicate that powdered metal brackets have a significantly greater tendency toward pitting corrosion from these pores. Additional work is needed to evaluate corrosion of powdered metals over a longer time frame and its affects if any on these pores.



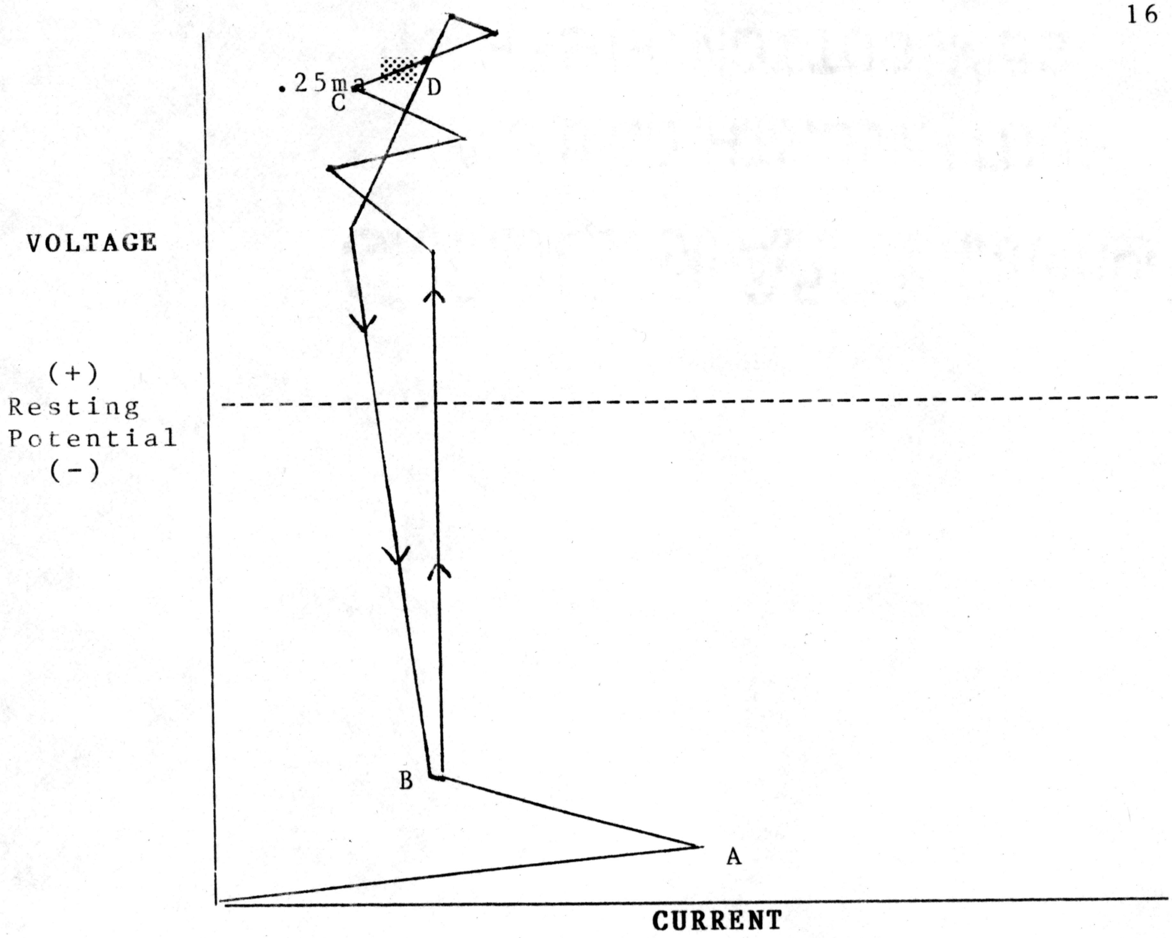
A=initial point of passivation
B=entire surface covered
C=initial breakdown of passivation layer
D=point of repassivation
Stippled Region= area of pitting corrosion

(fig.1--Standard Poteniodynamic Anodic Polarization Plot)



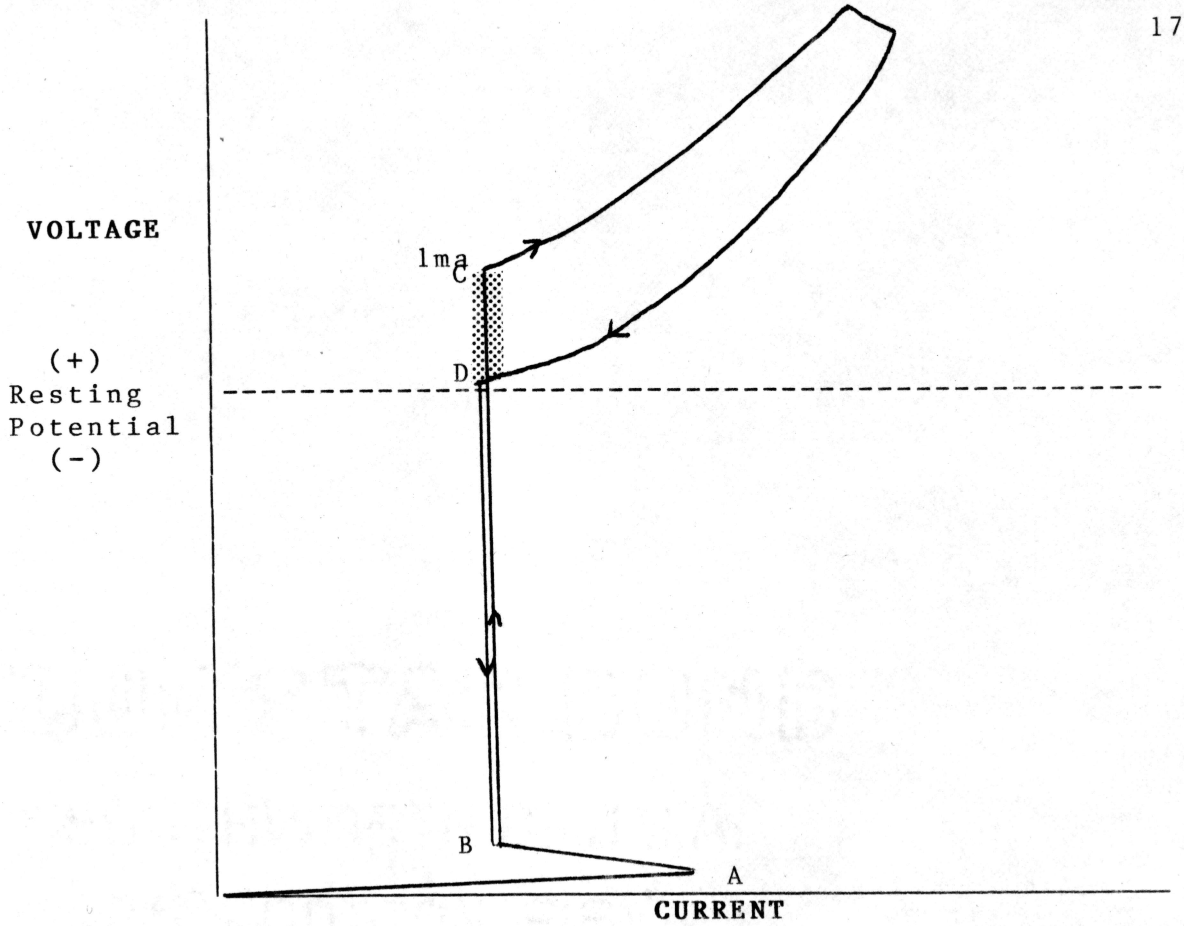
A=initial point of passivation
B=entire surface covered
C=initial breakdown of passivation layer
D=point of repassivation
Stippled Region=area of pitting corrosion

(fig.2--Standard Poteniodynamic Anodic Polarization Plot of 316-L powdered metal orthodontic bracket)



A=initial point of passivation
B=entire surface covered
C=initial breakdown of passivation layer
D=point of repassivation
Stippled Region=area of pitting corroison

(fig.3--Standard Poteniodynamic Anodic Polarization Plot of 316-L cast metal orthodontic bracket)



A=initial point of passivation
B=entire surface covered
C=initial breakdown of passivation layer
D=point of repassivation
Stippled Region=area of pitting corrosion

(fig.4--Standard Poteniodynamic Anodic Polarization Plot of 316-L cold worked orthodontic bracket)

(figure 5--Scanning electron micrograph showing an open pore on surface of powdered metal sample. Original magnification, X1000)

CHAPTER 6

Conclusions

1. The relative corrosion rate of the powdered metal brackets of $.2256_{mpy}$ is less than the cast or cold worked brackets. While the cast bracket has a slightly higher corrosion rate of $.4369_{mpy}$ than the powdered metal, it is much better than the cold worked sample. The cold worked sample shows the highest corrosion rate, 2.8135_{mpy} and thus would have the greatest potential for corrosion of the samples.
2. The current density at which the passivation layer breaks down, is lowest in the powdered metal sample(.11 microamps) with the cold worked samples showing a higher current density(1 microamp). This indicates that the powdered metal group would hold its passivation longer and have more resistance to corrosion.
3. The area of pitting corrosion which occurs after passivation has broken down and then reformed is the smallest in the cast metal group which indicates it has a greater resistance to pitting or crevice corrosion. The least resistance to pitting corrosion is found in the cold worked samples.
4. Open surface pores as seen on scanning electron

micrographs of the powdered metal brackets could present a possible corrosion problem in such parts over a long period of time, although in all probability not clinically significant.

Future Recomendations:

Potentiodynamic polarization measurements are valuable in predicting how a material will behave when exposed to a particular environment. It is a rapid **in vitro** technique to indicate the ability of a sample to protect itself from corrosion in a liquid environment. It must be realized that the conclusions given are based on an artificial method for corroding the samples. This is useful in predicting how a sample might behave in the oral environment but cannot replace long term studies where other factors may enter into the results. It would then follow that an **in vivo** experiment should be conducted to evaluate the material in a true oral environment. It would be possible to evaluate the staining of teeth which has been seen, and to also provide a clearer picture of the influence of the orthodontic brackets geometry or shape and its potential on increasing crevice corrosion.

In the background research for this paper an attempt was made to find a suitable artificial saliva to use for the liquid medium in order to duplicate the oral environment as accurately as possible. We were unable to find any standardized formula for artificial saliva which was consistent throughout the literature. We feel that it would be most useful to establish a standardized series of artificial salivas. These can then be used to provide a far greater consistency in dental research projects requiring artificial saliva.

Additional studies should also be conducted looking at the strength of the new powdered metal brackets as they compare to those currently in use. It is not known how or if strength is influenced by the injection molding process of these smaller parts. This could have a significant influence on their use for orthodontic brackets.

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Appendixes

Appendix-1.) Chromerics, 77 Dragon Court, Woburn, Mass. 01801

Appendix-2.) Princeton Applied Research, Analytical Instrument Division, Princeton, New Jersy.

Appendix-3.) California State Polytechnic University, Pomona; School of Science Electron Microscopy Center, 3801 West Temple, Pomona, CA 91768

Glossary

Anode--The electrode at which oxidation or corrosion occurs.

Anodic Polarization--Polarization of anode; i.e., the decrease in the initial anode potential resulting from current flow effects at or near the anode surface. The potential becomes more positive.

Austenitic--The name given to the face centered cubic crystal structure of ferrous metals. Ordinary iron and steel has this structure at elevated temperatures; also certain stainless steels (300) series have this structure at room temperature.

Corrosion--The destruction of a substance; usually metal, or its properties because of a reaction with is environment or surroundings.

Corrosion Potential--The potential that a corroding metal exhibits under specific conditions of concentraiton, time, temperature, aeration, velocity, etc.

Corrosion Rate--The average speed with which corrosion progresses. It may be reported as a weight loss per area divided by time or as thickness changes in milliinches per year.

Crevice Corrosion--Localized corrosion resulting from the formation of a concentration cell in a crevice formed between a metal and a nonmetal, or between two metal surfaces.

Current Density--Current flow for a standard surface size, measured as current divided by surface area.

Electrode--A metal in contact with an electrolyte which serves as a site where an electrical current enters the metal or leaves the metal to enter the solution.

Electrolyte--An ionic conductor, usually aqueous.

General Corrosion--Corrosion in a uniform manner.

Oxidation--Loss of electrons; as when a metal goes from the metallic state to the corroded state. Thus, when a metal reacts with oxygen, sulfur, etc., to form a compound as oxide, sulfide, etc., it is oxidized.

Passivation or Passivator--An inhibitor which changes the potential of a metal appreciably to a more cathodic or noble value.

Passive--the state of a metal when its behavior is much more noble (resists corrosion). This is a surface phenomenon.

Pitting--Highly localized corrosion resulting in deep penetration at only a few spots.

Polarization--The shift in electrode potential resulting from the effects of current flow, measured with respect to the reference or "zero-flow" potential. Usually caused by products formed or concentration changes in the electrolyte.

Potentiostat--An electronic device which maintains an electrode at a constant potential(Voltage).

Reduction--Gain of electrons; as when copper is electroplated on steel from a copper sulfate solution.