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SURFACE ANALYSIS OF TARNISHED DENTAL ALLOYS

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Abstract

Six crown and bridge alloys ranging in nobility between 25-63 wt % (18-45 at %) were analyzed by optical microscopy, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and secondary ion mass spectroscopy (SIMS), as well as by L*a*b* colorimetry before and after in vitro tarnishing in artificial saliva with and without additions of 0.00016, 0.016, and 1.6 % Na₂S with a rotating wheel apparatus. All alloys except the lowest of 18 at % changed colors to about the same degree after 72 h of tarnishing. All alloys decreased in L*, while increased in both a* and b*, thus appearing darker and with increased redness and yellowness. This was due to localized darkening and to other products. For all alloys except one, saliva without sulfide promoted color changes more severe than for saliva with 0.016 % Na₂S. For the most part, analysis by EDS was unable to detect differences between the tarnished films and the as-polished surfaces. SIMS analysis, however, showed changes in the substrate ion (Cu, Ag, Pd, and In) peak intensities. In most cases the intensities decreased and with the decrease greater with the sulfide-free saliva than with sulfide-containing. This indicated that sulfide promoted insoluble deposition of products. Changes in the Ag, Pd, and In peak intensities followed much the same pattern as with Cu. The as-polished surfaces, even though carefully prepared, showed much contamination in the form of organics, namely C, CH, N, NH, O, CHN, CN, as well as from Na, K, Ca, Si, S, Cl, and others. Most tarnished surfaces showed large increases in Na, K, and Ca, and with the sulfide-free saliva being more severe in this regard. The mass spectrum also showed peaks with atomic mass units in the range 55-58 related to only some of the tarnished surfaces.

KEY WORDS: scanning electron microscopy, energy dispersive and secondary ion mass spectroscopies, colorimetry, tarnish, corrosion, surface films, sulfidation, dental alloys, gold-content, saliva.

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Introduction

Dental alloys for crown and bridge uses are based upon the Au-Pd-Ag-Cu system. Low percentages of Pt, Zn, In, grain refiners, such as Ru and Ir, and others are also usually added. Alloys covering a wide range in compositions are available and used. Compositions with a minimum of 75 wt % nobility are referred to as the conventional gold alloys and were used in most crown and bridge situations up until the gold price skyrocketed. Lower gold-content alloys are now used extensively. Since tarnishing generally depends upon the nobility content in the alloys, it becomes important to evaluate and analyze the tarnishing of these alloys.

Alloy nobility, Ag/Cu and Pd/Au ratios, microstructure and others affect tarnishing. As alloy nobility decreases tarnishing usually increases.(1,3,11) High Ag/Cu ratios can have detrimental effects.(4) Tarnishing usually takes place on the Ag-rich phases while the Cu-rich phases remain unstained.(9) Increasing the Pd content, like increasing the Au-content, increases tarnish resistance.(6) This effect, though, is often greater with palladium. However, increasing the Pd content too much can reverse the Pd effects and increase tarnishing again. Microstructurally, small additions of Pd to Au-Ag-Cu alloys enrich the surface layers in Pd thereby increasing the resistance to tarnishing.(10) Multiphasal microstructures increase susceptibility to tarnishing via microgalvanic coupling. Single phase solid solution annealed microstructures show increased resistance to tarnishing.(1)

Spectroscopic techniques used in analyzing alloy surface features including adhered film characteristics have included x-ray microprobe(4, 9), EDS(2), Auger electron spectroscopy(AES)(5), and x-ray photoelectron spectroscopy.(10) Both AES and ESCA are capable of chemically analyzing the top outermost layers of surfaces, whereas microprobe and EDS penetrate too deeply into the bulk to be considered solely as techniques for surface analysis. This distinction is particularly of interest for the tarnished films on dental alloys, since film thicknesses are most often very thin thereby being easily penetrated by the microprobe and EDS beams. Their analyses are likely to include substrate characteristics and therefore

not be representative of only the surface films. SIMS is another technique ideally suited for surface analysis. The surface is bombarded with a beam of ions, such as argon or oxygen. The very top outermost surface ions are ejected, collected, and analyzed by a mass analyzer. Collected mass intensity vs atomic mass unit plots are generated for both positive and negative ions.(8)

The objective of this project was to evaluate and compare the tarnishing, and to analyze the surface films of a number of low-gold alloys currently used for crown and bridge applications. The tarnishing reactions were to involve sulfidations, since intraorally, dental alloys tarnish via reactions with sulfur.(12) In vitro tarnishing was to be generated by a rotating wheel apparatus, which is thought to simulate intraoral tarnish.(7) Evaluations for the degree of tarnish were to be followed quantitatively by colorimetry methods (1) and the films were to be analyzed chemically by SIMS. This is the first time, as well as can be determined, that SIMS was used in analyzing the tarnished surface films on dental alloys.

Materials and Methods

Table 1 lists the six crown and bridge alloys used, their manufacturers' stated compositions, and their atomic and weight percent nobilities (Au, Pt and Pd contents). The alloys were centrifugally

Alloy(*)	Wt %				Nobility	
	Au	Pd	Ag	Cu	Wt %	At %
Stern 20 (S)	59.5	4	25	11.5	63.5	45.1
Tiffany (S)	50	4	25	21	54	34.1
Sunrise (S)	39	6(+)	41	13	46	30.7
Pentron 20 (P)	20	20	40	bal(++)	40	32.2
Econocast (P)	26	10		bal	36	18.3
Albacast (J)	-	25	70	5	25	24.3

(*) manufacturers: (S)=Sterngold, (P)=Pentron, and (J)=Jelenko;(**) Cu taken to be the difference (+) with 1 % Pt; (++) balance Cu and In.

cast inductively into gypsum bonded molds by the lost wax process and at temperatures recommended by their manufacturers. Two castings were made per alloy, except for Sunrise and Albacast, in which four each were made. Five minutes following casting the alloys were water quenched. The 12 mm dia x 2 mm thick samples were ground and polished metallographically on both faces to a 1/4 μ m diamond finish. Microhardness marks were made on the surfaces so that the same areas on the samples were able to be repositioned into the field of view before and after tarnishing. The alloy samples were etched with a solution containing 1 part of a 20% solution of potassium cyanide and 1 part of a 20% solution of ammonium persulfate to better reveal their underlying structures. Both optical microscopy and a Cambridge Mark IV Stereoscan scanning electron microscope were used.

Following repolishing of the etched surfaces, the acetone degreased surfaces were viewed by optical microscopy and SEM, and analyzed by EDS and SIMS. A Princeton Gamma Tech energy dispersive x-ray spectrometer detected and semi-quantitatively analyzed the elemental contents. An NBS Frame C computer program analyzed composition by a standardless procedure. Corrections were taken for atomic number, absorbance, and fluorescence(ZAF). All analyses collected x-ray counts for 500 sec on each of two different areas. Each different appearing microstructural region on the as-polished surfaces was analyzed. An ion gun source and quadrupole mass analyzer of a Kratos SIMS unit were attached ("bolted on") to the column of the SEM. The ion beam diameter was of the order of 1 mm so that the SIMS analyses were representative of the microstructure as a whole instead of only selected microstructural components as done with much smaller beam diameters, and as can be done with EDS. The sample current and voltage were kept constant at about 1.2 nA and 1.3 kV so that comparisons could be made among the different analyses. Both positive and negative spectra were taken immediately after positioning sample surface under argon beam. Spectra up to 120 atomic mass units took about 15 minutes. Depth profiling was not practical with this static SIMS mode since hours of ion etching produced very little changes in spectrum levels. Much higher current levels are required to alter surfaces by a bombarding ion beam.

The alloys were tarnished for times up to 72 hours with a cyclic immersion apparatus similar to ones already used (12). No cloths were used for wiping across the alloy surfaces as done with some dental alloy tarnishing procedures. The unit consisted of plexiglas wheels onto which the sample alloys were held. A shaft connected to a constant rpm motor rotated the samples at 1 rpm through the tarnishing solutions positioned beneath the revolving wheels. The levels of the solutions were so adjusted that the alloys made contact with the solutions for 15 sec/rev. A plexiglas cover enclosing the apparatus prevented most of the solution evaporation that otherwise would have occurred due to air circulation and local environmental conditions. Throughout the 72 h tests, no noticeable solution loss occurred. One sample of each alloy was rotated through an artificial saliva solution (1) listed in Table 2 without added sulfide, while additional samples

TABLE 2
Composition of Artificial Saliva*

Ingredient	Amount(gm)
NaCl	0.4
KCl	0.4
CaCl ₂ · 2H ₂ O	0.795
NaH ₂ PO ₄ · H ₂ O	0.69
urea	1.0
H ₂ O	1000

*0.005 gm Na₂S · 9H₂O also usually added

were rotated through the artificial saliva with added 0.016 % Na₂S. Samples of Sunrise and Albacast were also rotated through 0.00016 %, and 1.6 % Na₂S containing saliva. Human saliva contains, on the average, about 0.001 % S and is between the two lower Na₂S concentrations used. A higher sulfide-containing saliva was also used to accelerate the tarnishing and to simulate the higher sulfide concentrations likely to accumulate on surfaces and in crevices. Following completion of the tarnishing tests, the samples were rinsed with ample quantities of distilled and deionized water and dried with a mild stream of purified air. The tarnished alloy surfaces were analyzed by optical microscopy, SEM, and by SIMS. For the most part, EDS proved to be ineffective in analyzing the tarnished films due to their thinness.

Alloy color was quantitatively evaluated by the Commission Internationale de l'Eclairage (C.I.E.) L*a*b* system by using a Minolta chroma meter CR-100. The L*a*b* values were read directly from the digital readout. The L*a*b* color space is characterized by a three-dimensional coordinate system. By definition the L* axis is a measure of the brightness, with L* = 100 being white and L* = 0 being black, and with the +a*, -a*, +b*, and -b* axes corresponding to red, green, yellow, and blue, respectively. Alloy tarnish was evaluated by comparing the alloys' color before and after exposure to the tarnishing solutions. The total amount of discoloration was calculated from the following,

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (1)$$

where ΔE^* is a vector denoting total color change and ΔL^* , Δa^* , and Δb^* are the changes in the color coordinates. A ΔE^* value of $\frac{1}{2}$ to 1 is just discernible with the human eye. The means from four color readings for each of L*, a*, and b* were used in calculating the color change vector per condition.

Results

Figure 1 presents the total color change vectors ΔE^* vs tarnishing times for the six alloys cyclicly exposed to 0.016 % Na₂S containing saliva. The color change rates were greatest at short times and with Econocast changing color the most. Standard deviations were small, ranging from 0 to about 0.3, and are not shown in accompanying figures to preserve clarity. Analyses of the component color vectors (fig 2) indicated that all alloys decreased in L* and increased in a* and b* after tarnishing, thus appearing darker but with increased redness and yellowness.

Figure 3 presents the color change vectors vs atomic nobility for the six alloys exposed to both the artificial saliva without sulfide and with 0.016 % sodium sulfide. The lowest nobility alloy of 18 % tarnished more than the other alloys. Even the alloy with about 25 % noble metals tarnished only slightly more than higher nobility alloys. Tiffany, however, with 35 % nobility increased tarnishing in the sulfide solution. All alloys except Tiffany tarnished more in saliva without sulfide. The color analysis for Sunrise exposed to artificial saliva with and without three concen-

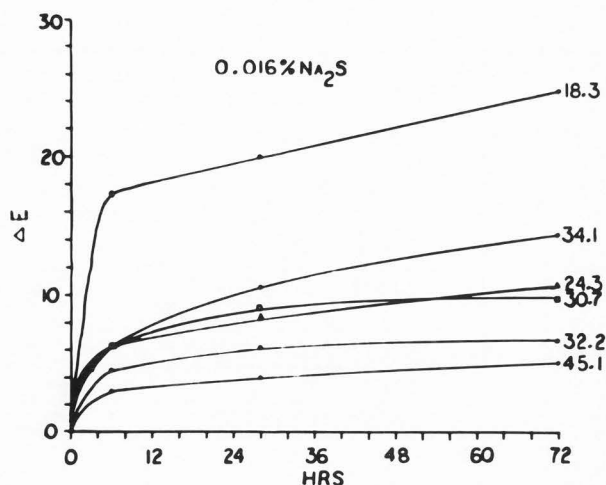


Figure 1. Total color change vector ΔE^* vs time plots for six dental alloys tarnished in artificial saliva. Alloys are identified by atomic nobility percent (see Table 1).

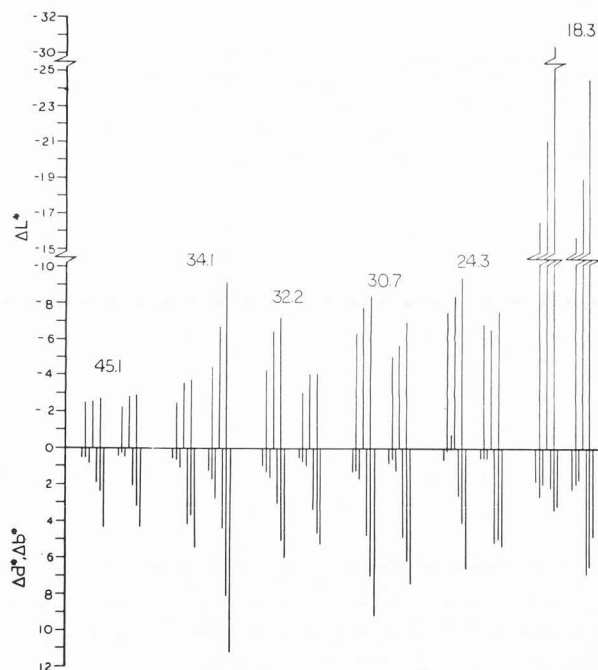


Figure 2. Color vectors (ΔL^* , Δa^* , and Δb^*) vs alloy atomic nobility (see Table 1). Each alloy represents two sets of ΔL^* values (3 values each) representing sulfide-free saliva (left) and 0.016 % Na₂S-containing saliva (right). Each set represents tarnishing times of 12, 28, and 72 h (left to right). Immediately below and to the left are the Δa^* values and to the right the Δb^* values.

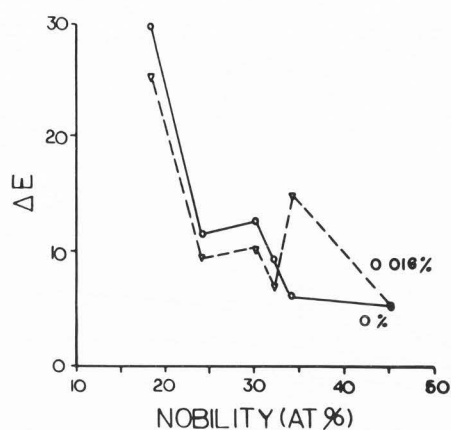


Figure 3. Color change vector ΔE^* vs atomic nobility for six dental alloys (see Table 1) tarnished in both sulfide-free saliva and 0.016 % Na_2S -containing saliva

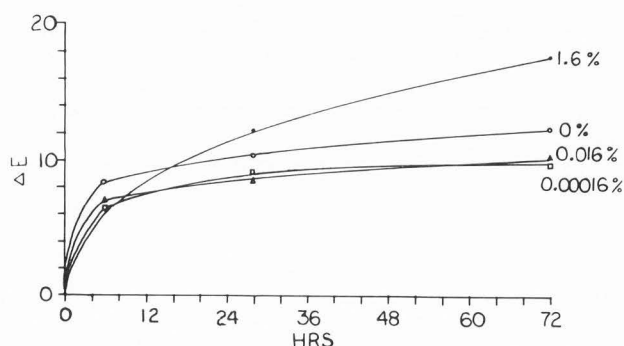


Figure 4. Color change vector ΔE^* vs time plots for the alloy Sunrise tarnished in sulfide-free saliva and with 0.00016, 0.016, and 1.6 % Na_2S .

trations of added sodium sulfide is shown in Figure 4. The two lower sulfide concentrations tarnished less than with saliva without sulfide, while the highest sulfide concentration generated increased tarnishing.

Figures 5-10 present micrographs of the etched microstructures for Sterngold 20, Tiffany, Sunrise, Pentron 20, Econocast, and Albacast, respectively. The grain and dendritic structures can be easily seen with most alloys, while multiphasal structures are evident with Pentron 20, Econocast, and Albacast. For the as-polished surfaces, all alloys appeared homogeneous except Pentron 20 and Econocast, where at least two phases were detected with each. Compositional analyses by EDS for the as-polished surfaces are presented in Table 3.

Figures 11-16 show the alloy surfaces after 72 h of tarnishing. All surfaces are severely darkened locally as well as deposited with light-appearing products. Figure 17 shows a higher

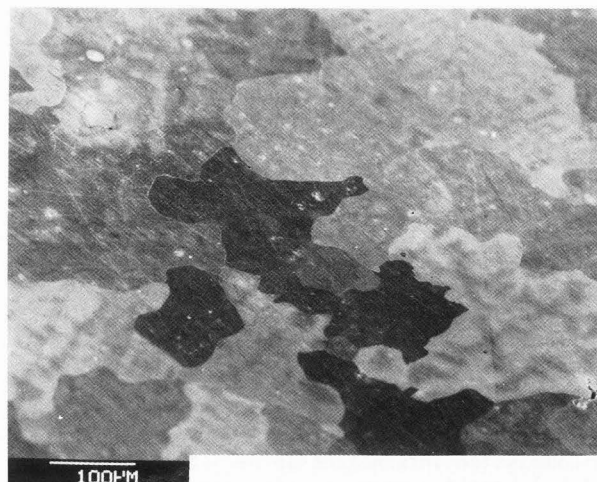


Figure 5. SEM micrograph of etched Stern 20.

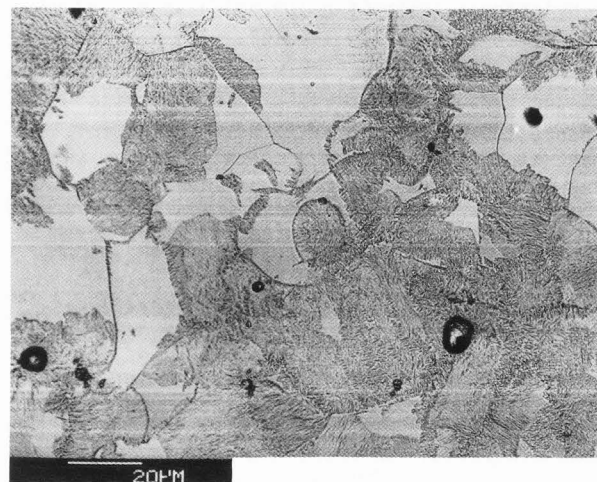


Figure 6. SEM micrograph of etched Tiffany.

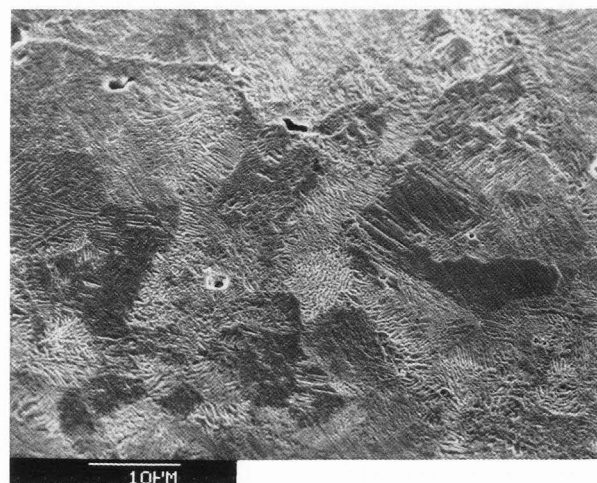


Figure 7. SEM micrograph of etched Sunrise.

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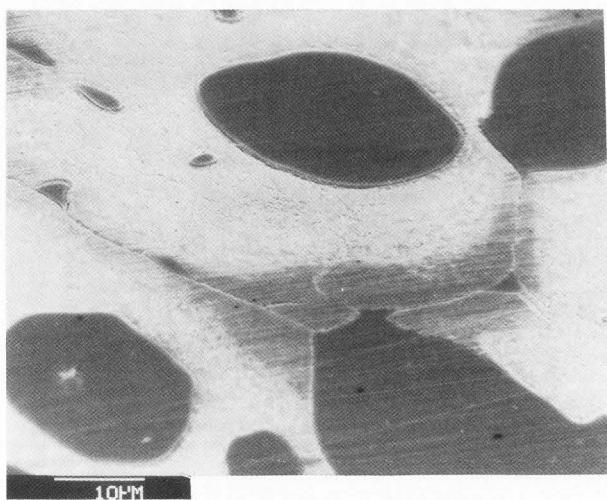


Figure 8. SEM micrograph of etched Pentron 20.

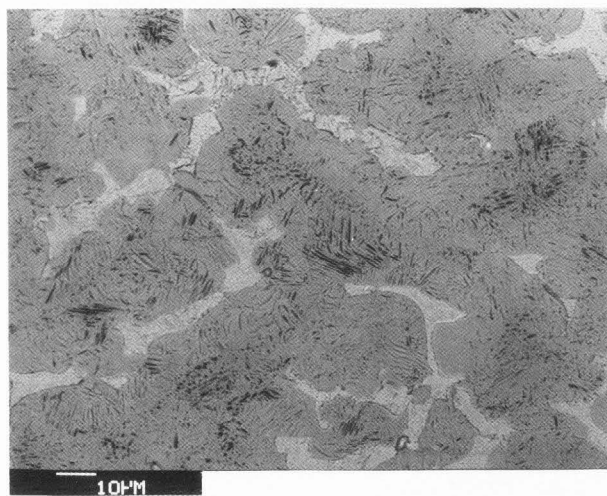


Figure 9. SEM micrograph of etched Econocast.

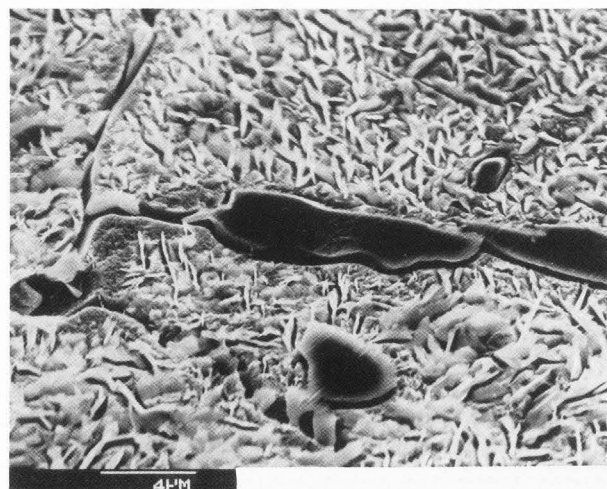


Figure 10. SEM micrograph of etched Albacast.

TABLE 3
EDS Analysis of As-Polished Alloys (wt %)

Alloy	Au	Pt	Pd	Ag	Cu	Rb	In	Zn
Stern 20 matrix	61.2	1.7	5.5	23.5	5.6	2.0	0	0.5
Tiffany matrix	54.0	1.7	4.3	25.6	11.5	1.6	0	1.4
Sunrise matrix	40.8	0.8	8.3	43.0	5.2	1.6	0	0.3
Pentron matrix	23.0	0.5	7.5	54.2	0.6	1.2	7.5	0.5
dk phase	9.0	0	40.9	18.3	0.4	0.2	30.2	1.0
Econocast matrix	31.2	0	17.1	13.8	35.9	1.1	0	0.9
lt phase	22.7	0.4	3.4	64.4	7.3	1.3	0	0.5
Albacast matrix	0.4	0.	24.1	70.5	0.	0.9	1.7	1.3

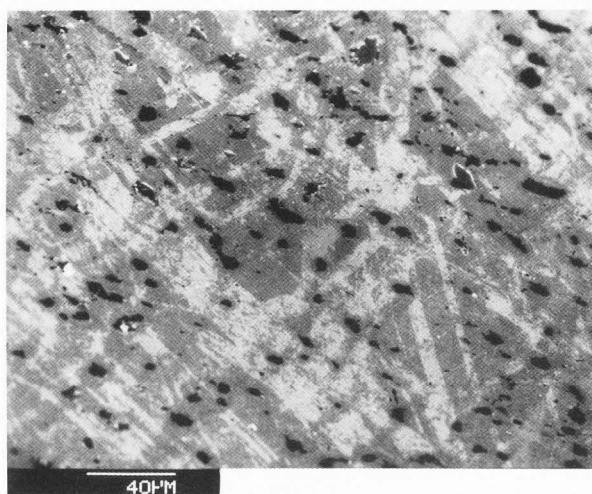


Figure 11. SEM micrograph of Stern 20 tarnished in 0.016 % Na₂S-containing artificial saliva.

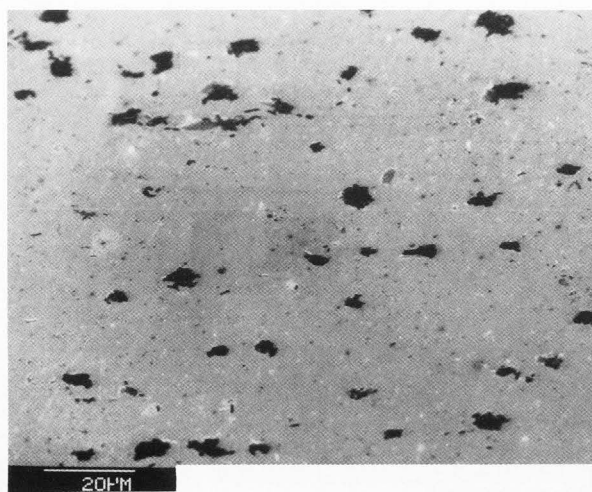


Figure 12. SEM micrograph of Tiffany tarnished in 0.016 % Na₂S-containing artificial saliva.

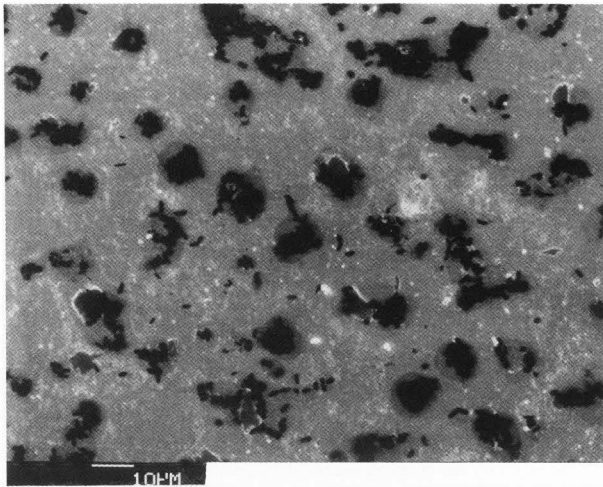


Figure 13. SEM micrograph of Sunrise tarnished in 0.016 % Na_2S -containing artificial saliva.

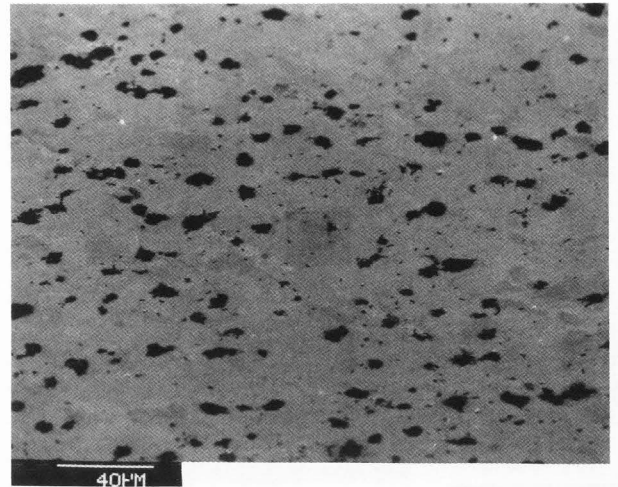


Figure 16. SEM micrograph of Albacast tarnished in 0.016 % Na_2S -containing artificial saliva.

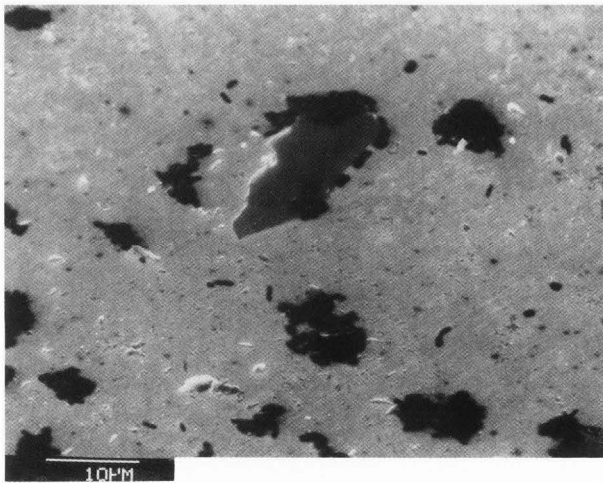


Figure 14. SEM micrograph of Pentron 20 tarnished in 0.016 % Na_2S -containing artificial saliva.

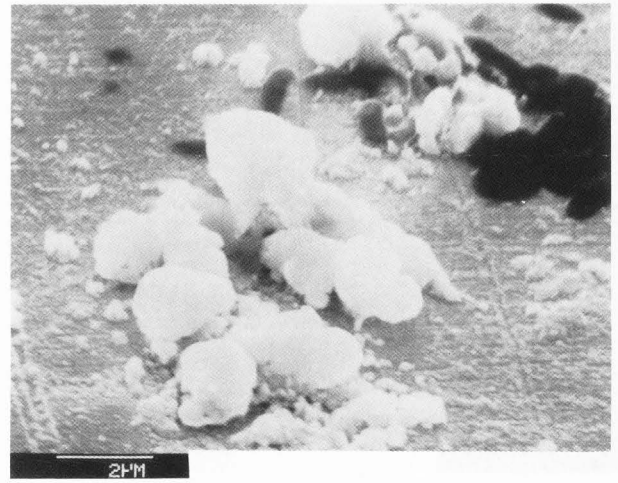


Figure 17. SEM micrograph of Econocast tarnished in sulfide-containing artificial saliva.

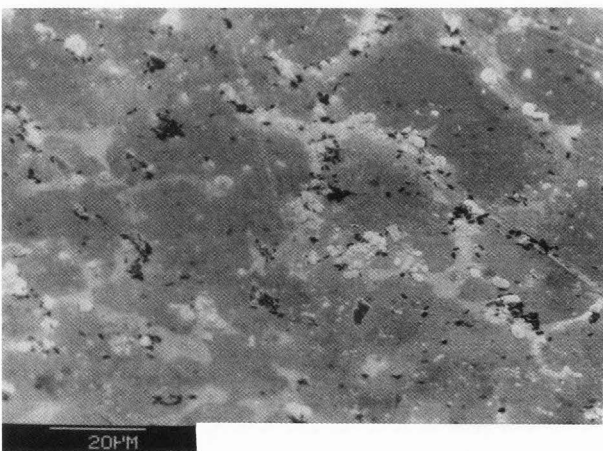


Figure 15. SEM micrograph of Econocast tarnished in 0.016 % Na_2S -containing artificial saliva.

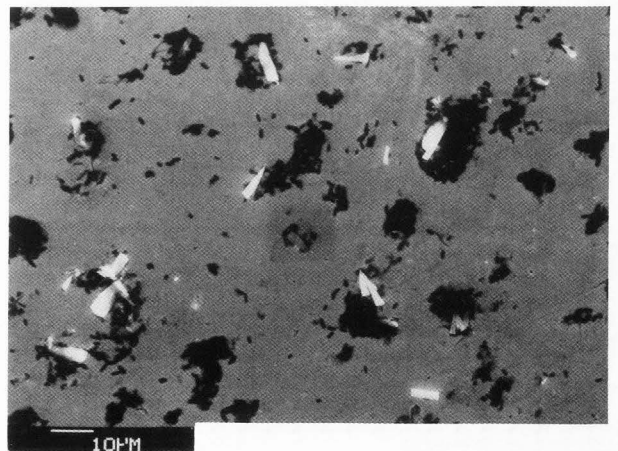


Figure 18. SEM micrograph of Sunrise tarnished in sulfide-free artificial saliva.

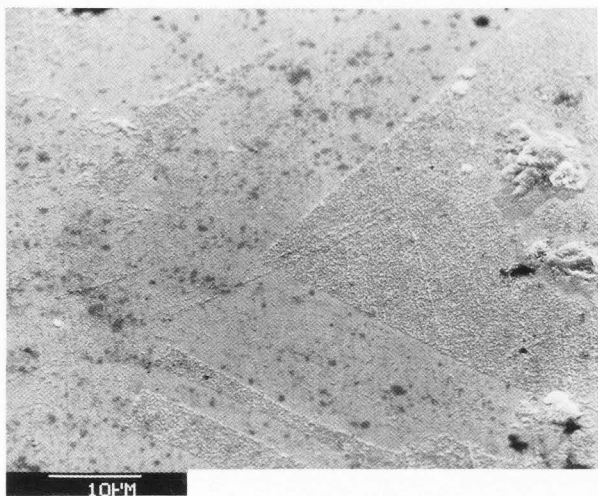


Figure 19. SEM micrograph of Sunrise tarnished in 1.6 % Na₂S-containing artificial saliva.

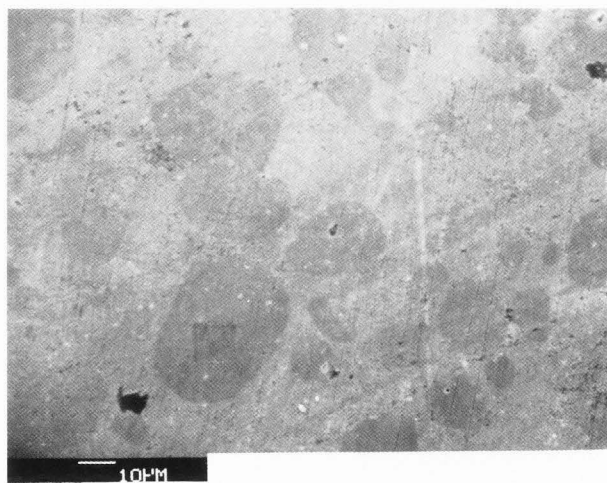


Figure 20. SEM micrograph of Pentron 20 tarnished for 16 h in 0.016 % Na₂S-containing saliva.

magnification of these products on Econocast. Micrographs for Sunrise tarnished in artificial saliva without sulfide and with added 1.6 % Na₂S are shown in Figures 18 and 19. The sulfide-free saliva exposed surface (Figs 13 and 18) contains less of the light-appearing products, while the high sulfide-exposed surface is overlaid with a thicker film of products. Figure 20 presents the 16 h tarnished surface for Pentron 20. Energy dispersive spectroscopy analysis of all tarnished surfaces, indicated very similar spectra to only the as-polished surfaces. Slight differences in intensity of the various substrate elements occurred, but this was not convincing enough in distinguishing between tarnished and untarnished surfaces. Besides, EDS failed to show elements, such as, chlorine, sulfur, and phosphorus, likely to be contained within the tarnished films on the alloys.

Figures 21-26 present positive SIMS spectra (intensity-counts vs atomic mass units) for the six alloys and each in the as-polished, sulfide tarnished and sulfide-free saliva tarnished conditions. Analyses were conducted up to atomic mass unit (amu) of 120, which means that Au and Pt were not included in the analyses. However, the other substrate ions of Cu (amu=63,65), Ag(107, 109), Pd (108, 110), and In (114) were identified, as well as the non substrate ions of C (12), N (14), O (16), Na (23), Si (28), K (39), Ca (40), and others. Combinations were also identified, including CH (13), NH (14), CHN (27), CN₂H₃(43) and others. Several observations are to be noted. The as-polished surfaces showed the least contamination even though large Na peaks as well as peaks for K, Ca, C, N, Si, and others were identified. Peak intensities for substrate ions, particularly Cu, but also for Ag, Pd, and In, were generally highest for the as-polished surfaces. The sulfide-free saliva tarnished surfaces for most alloys showed higher Na and K peak intensities. Corrosion products with atomic mass units in the 55-58 range occurred with some of the alloys.

The negative SIMS spectra for Tiffany is shown in Figure 27 for as-polished, sulfide tarnished, and sulfide-free saliva tarnished surfaces. Spectrum for the other alloys were similar to the ones for Tiffany. It is noted that the as-polished surfaces show as high or even

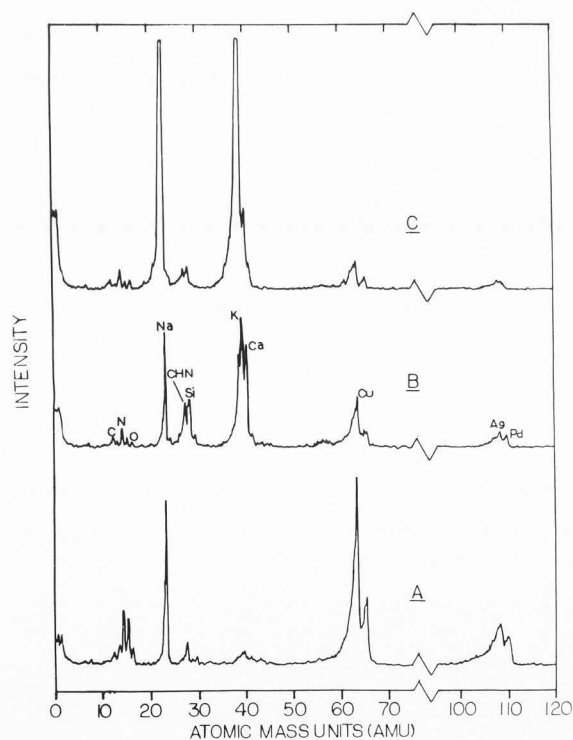


Figure 21. Positive SIMS spectrum for Stern 20 as-polished (A), and tarnished for 72 h with 0.016 % Na₂S saliva (B), and with S⁻-free saliva (C).

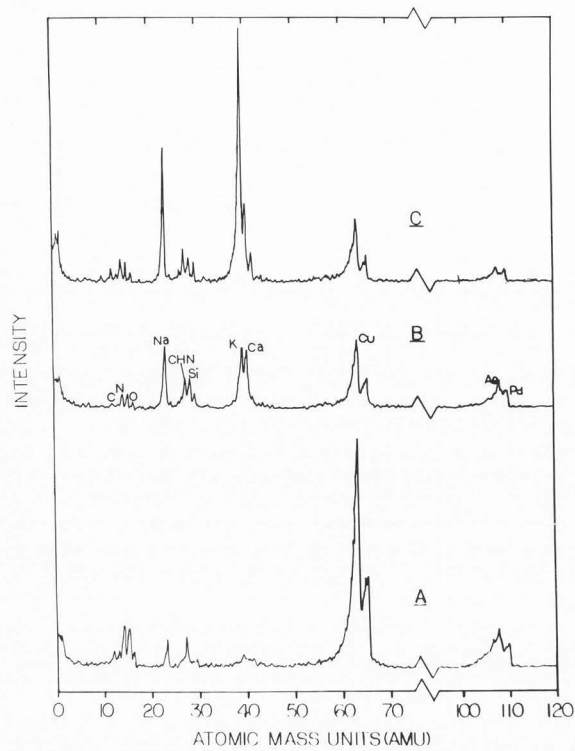


Figure 22. Positive SIMS spectrum for Tiffany. A, B, C as in Figure 21.

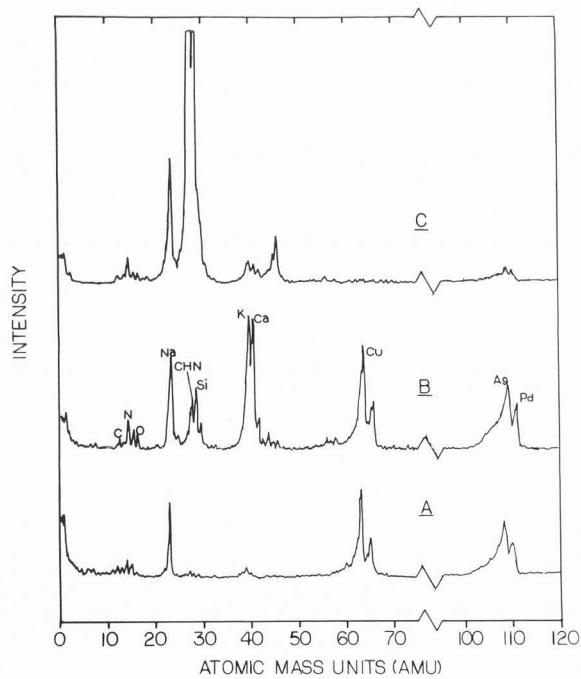


Figure 23. Positive SIMS spectrum for Sunrise as-polished (A), and tarnished for 72 h in 0.016 % Na_2S saliva (B), and in S-free saliva (C).

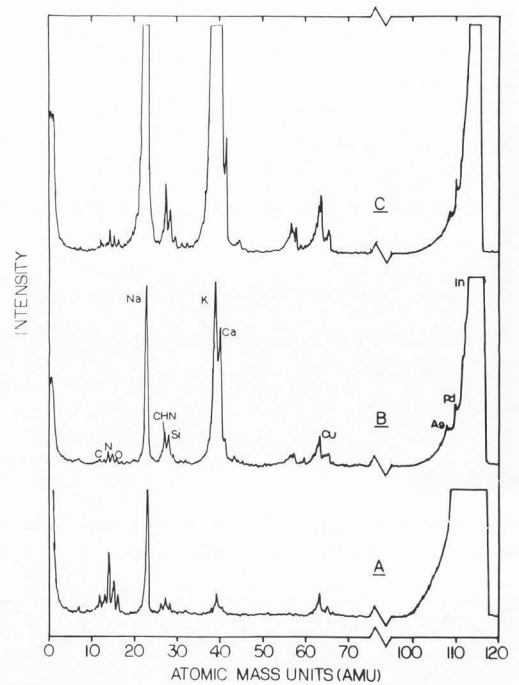


Figure 24. Positive SIMS spectrum for Pentron 20 with the three conditions listed in Figure 23.

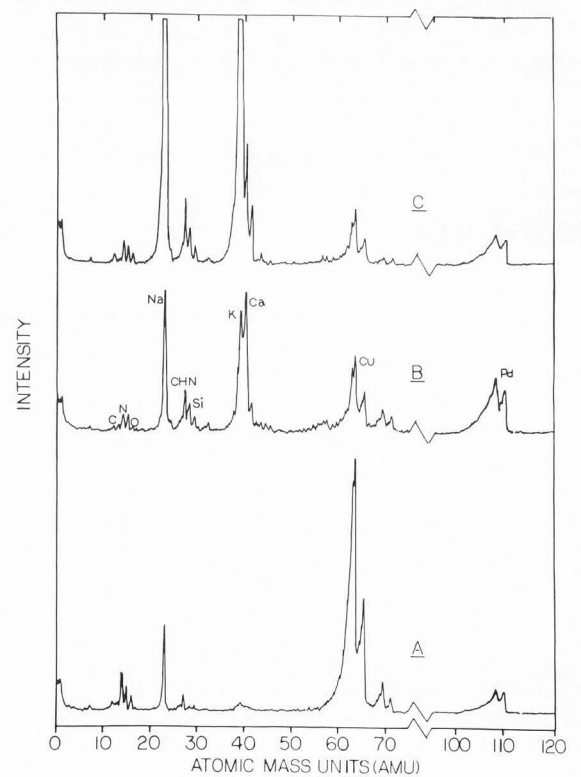


Figure 25. Positive SIMS spectrum for Econocast and with the three conditions listed in Figure 23.

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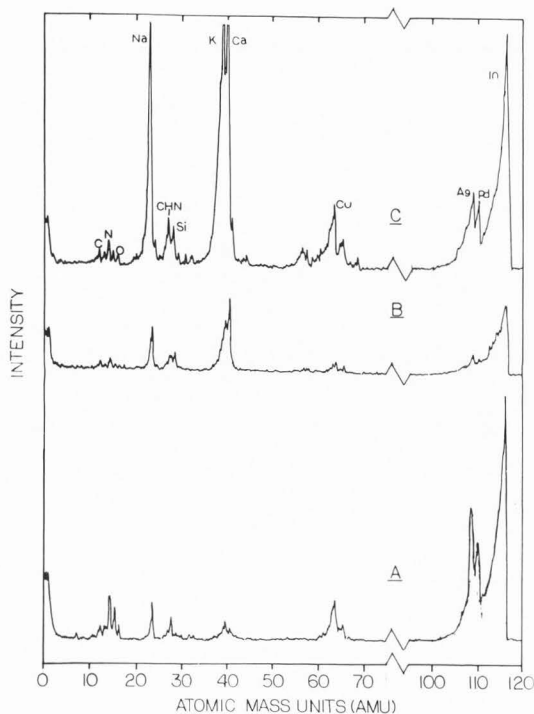


Figure 26. Positive SIMS spectrum for Albacast. A, B, C as in Figure 23.

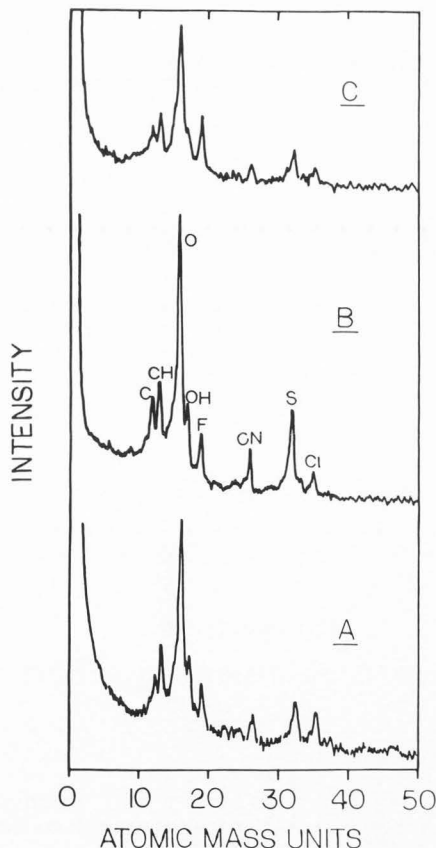


Figure 27. Negative SIMS spectrum for Tiffany. A, B, C as in Figure 23.

higher peak intensities for C, CH, O, OH, F, and CN. The S peak intensity for the 0.016 % Na_2S tarnished surface is higher than for either as-polished or sulfide-free saliva tarnished surfaces. Chlorine was detected for all conditions of the alloy, even on the as-polished surface.

Discussion

The four alloys of Sterngold 20, Tiffany, Sunrise, and Econocast all showed, for the most part, significant decreases in the intensities of the Cu peaks in going from the as-polished surfaces to the saliva (either with or without S) tarnished surfaces. This implied that tarnished films composed partly of copper formed on the surfaces. In comparing the Cu intensities formed in the sulfide-free saliva to the sulfide-containing saliva, it is noticed that the copper intensities were less with the sulfide-free saliva. In fact for Sunrise the Cu intensity in the sulfide-free saliva was negligible. This implied that the adherent products of tarnishing were composed of less Cu when formed in the sulfide-free saliva. It is very likely the Cu participating in the tarnishing reactions became solubilized. The higher Cu intensity for Sunrise in sulfide-containing saliva may mean the increased susceptibility for Cu to form adherent sulfidation products. For Sterngold 20, Tiffany, and Econocast, the tarnished films were likely composed only partly by adherent Cu products. For Pentron 20, both saliva types indicated increased Cu intensities after tarnishing, suggesting an increased proportion of Cu products to be contained within the adherent tarnished films. Albacast indicated increased Cu intensities in sulfide-free saliva, while decreased intensities in sulfide-containing saliva. Again this shows the possible dual nature the tarnishing products take depending upon solubility considerations. For Sterngold 20 and Tiffany, similar decreases with Ag and Pd occurred on the tarnished surfaces as with Cu, indicating decreased participation of these elements in the adherent tarnished films. For Sunrise and Econocast, increases in the Ag and Pd intensities occurred in the sulfide-containing saliva. This may indicate that Ag participated more in sulfidation tarnishing, while Pd may have become enriched in the outermost layers. Pentron 20 and Albacast also decreased in Ag and Pd intensities on the tarnished surfaces, as well as in In intensity likely indicating soluble products to have formed or a decreased participation of these elements with the tarnishing reactions.

All as-polished surfaces indicated difficulty in obtaining uncontaminated surfaces. In spite of the tedious efforts utilized in preparing the as-polished surfaces, including ultrasonics in detergent solution followed by acetone and carbon tetrachloride degreasing, all as-polished surfaces showed concentrations of organics, including C, CH, N, NH, O, CHN, in some instances CN_2H_3 (amu-43) and possibly others from the positive SIMS data, while the negative spectrum indicated in addition, OH, and CN. Other contaminations included Na, Si, K, Ca, F, Cl, and others. Sodium intensities from some surfaces were highest. This points to the need in obtaining uncontaminated surfaces prior to

tarnishing in order to better define the tarnishing reactions. Current experiments are utilizing glow-discharged treated alloy surfaces.

The tarnished surfaces indicated changes in the intensities of not only substrate ions, as indicated above, but also of the non-substrate ions. The most notable changes occurred with Na, K, and Ca, as well as smaller increases with Si, CHN, and other organics in selected instances. The surfaces exposed to the sulfide-free saliva indicated greater intensities for Na, K, and in some instances with Ca. Sunrise showed increased Si intensities and lower K and Ca intensities in the sulfide-free saliva. A need exists to better characterize these non-substrate ions with the tarnishing reactions.

Additional peaks ($amu=55-58$) occurred in the positive spectrum for the tarnished surfaces that did not occur on the as-polished surfaces. These were most noticeable for Pentron 20, Albacast, and Econocast, while less noticeable with Sunrise, Sterngold 20, and Tiffany. The identification of these products remained uncertain. Albacast tarnished in the sulfide-free saliva also indicated products with atomic mass units of 66-68, while Econocast in the as-polished and tarnished conditions showed additional peaks at $amu=69$ and 71 .

Relationship of tarnishing to microstructure has only been established with certainty with one alloy, that being Econocast (compare figs 9 and 15). The light-appearing Ag-rich phase in contrast to the Cu- and Au-rich matrix is the more prone to corrosion. With all other alloys, the 72 h tarnished surfaces showed no resemblance to their microstructures. The underlying microstructures were obscured with adherent tarnished films. This may be expected with Sterngold 20, Tiffany, and Sunrise, but not with Pentron 20 and Albacast, the latter two alloys being multiphase structures. The 16 h tarnished surface for Pentron 20 showed some resemblance to structure. The light-appearing Ag-rich matrix has become noticeably tarnished (fig 20). At 16 h, Albacast showed delineation of the elongated second phase inclusions. Even though not detected and analyzed by the EDS analysis (Table 3), this second phase is likely Pd- and Cu-rich (9). Differences in tarnishing resistance due to compositional differences generated by dendritic segregations and coring is also expected to have occurred. Non-compositional factors, such as, porosity (see Fig 7 for typical concentrations) may have partly contributed to the tarnishing caused by the dark patches but is unlikely to have been totally responsible in forming the dark areas detected in Figures 11-16.

The two lower sulfide-containing salivas yielded less tarnish with Sunrise than sulfide-free saliva (fig 4). This was unexpected since traditionally sulfide has been associated with dental tarnish. Partial compensation of the surface darkening caused by the localized dark patches may have been partially compensated by the light-appearing products. Sunrise exposed to saliva, containing 0.016 % Na_2S , contained more of the light products than after exposure to sulfide-free saliva (compare figs 13, and 18). With the higher concentration of 1.6 % sulfide, increased tarnishing again occurred at time longer than

about 15 hrs which was likely due to the increased accumulation of products (fig 19). It should be noted that more color change has been detected with a number of low-gold alloys when tarnished with an artificial saliva than with 0.5 % Na_2S solution.(1)

The sulfur detected on Tiffany exposed to sulfide-containing saliva was about two times the intensity as detected on surface exposed to sulfide-free saliva and to as-polished surface. Higher levels may have been expected on sulfide-exposed surfaces since sulfidation products, such as Ag_2S , have been related to dental alloy tarnishing. Besides, measured S/Ag concentration ratios within the tarnished films have indicated (10) ratios up to 100 and more. Even though many of the sulfide compounds expected to form have low solubility constants, one reason for the lower sulfur concentrations than expected may have been due to the formation of soluble products. This supports the viewpoint presented earlier for decreased Cu and Ag SIMS intensity peaks on tarnished films. Tiffany also increased color change in sulfide-containing saliva. The effects of organics and non substrate ions in affecting color may have been greater here.

Conclusions

1. SEM analysis of alloys tarnished by either a sulfide-free or a sulfide-containing saliva indicated both localized areas of darkening and light-appearing precipitates.

2. $L^*a^*b^*$ colorimetry analysis of the tarnished alloys indicated that all alloys except the lowest nobility alloy of 18 at % tarnished to about the same degree. All alloys appeared darker and with increased redness and yellowness after tarnishing.

3. SIMS analyses showed decreased substrate ion peak intensities for a number of alloy-solution combinations, while increased intensities for other combinations. Solubility was considered to be a major factor in this regard. Sulfide-free saliva for the most part generated lower substrate ion film concentrations than sulfide-containing saliva.

4. Organics were detected by SIMS on all surfaces. Sodium contamination was greatest on the as-polished surfaces. The tarnished surfaces showed increased intensities for Na, K, and Ca, and with the sulfide-free saliva more effective than the sulfide-containing saliva.

5. Peaks occurring in the mass spectrum between atomic mass units of 55 to 58 were due to the reactions of tarnishing.

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Discussion with Reviewers

R.M. German: The rotating wheel tarnish apparatus leads to selective evaporation of ions (like S) over time. This gives poor reproducibility since the results depend on factors such as air circulation, ambient temperature and relative humidity. What are the authors' thoughts on variations induced by these factors, how significant are these effects and what measures were taken to control the test reproducibility?
 Authors: Variations in environmental conditions are capable of affecting the reproducibility with the colorimetry analyses due to solution evaporation and hence changes in solution concentrations. Without safeguards and scrutiny over the imposed conditions of the tests, color vectors are likely to be changed at least in proportion to the changes in solution concentrations. For tarnishing solutions containing highly mobile species like S⁻ and bicarbonate which are easily converted to the gaseous phase, colorimetry data is also expected to be affected at even higher levels. These factors, however, were originally designed to be kept to a minimum by conducting the tarnish tests in a controlled temperature (23± 1°C) and relative humidity (55 ± 2%) area as well as by enclosing the entire rotating wheel apparatus with a plexiglas cover. The apparatus shown in Figure 28 illustrates both the rotating wheels and containers for holding the various tarnishing solutions. The enclosing cover is not shown for clarity.

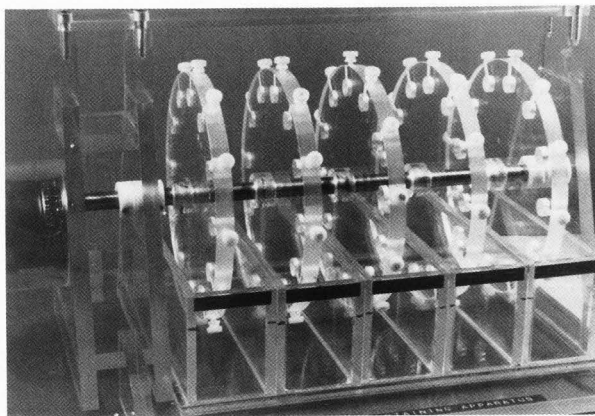


Figure 28. Rotating wheel apparatus.

A. Acharya: Why did the Cu contents of Sterngold, Tiffany, and Sunrise alloy differ by a factor of 2 or more between the manufacturers' specifications in Table 1 and EDS analysis in Table 3?
 Authors: Variations by several percent in Au, Pd, and Ag occurred between the EDS compositional analysis and manufacturers' stated compositions. With the standardless EDS methods used, accuracies were no more than ±2-3 %. Larger variations occurred with Cu because of the difference method used to arrive at the manufacturers' Cu contents given in Table 1. The minor alloying elements of Rb, Zn, and In detected by EDS and listed in Table 3 were not available from the compositions off of the package labels. Hence, in arriving at the Cu contents given in Table 1, higher percentages than actual were obtained due to not including the minor alloying elements.

J.L. Sandrik: Can an explanation be offered for the behaviour shown in Figure 3 where 0.016 and 0.00016% Na₂S resulted in lower ΔE values than non-sulfide containing artificial saliva?
 Authors: The potential exists for artificial saliva to form a variety of tarnishing species due to its complexity in composition. Artificial saliva with or without added sulfide generated dark patches across the surfaces as well as lighter products. With added sulfide, the concentrations of the inter-dark patch product deposition increased. It is believed that these lighter products led to the measured decreased darkening as shown by the changes in the color vectors.

G.W. Marshall: The negative SIMS spectra appear to show little change in S content. How can that be explained in terms of the wide spread theory that S is responsible for much of the tarnish?
 Authors: It is agreed that the S levels detected by the negative SIMS analysis on the tarnished surfaces were lower than expected. A possible explanation may be due to the analysis of only the very outermost layers of the films by the static SIMS mode technique used. It may be that increased concentrations of S are in fact accumulated at distances nearer to the substrate alloy. Only a dynamic SIMS mode technique would, however, prove or disprove this hypothesis by depth profiling.