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Original Research Article

Does Bleaching Agent Have A Detrimental Corrosive Effect On Dental Casting Alloys?

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ABSTRACT

Aim: The effect of bleaching agent on corrosion behavior and surface roughness of fixed prosthodontics alloys was investigated.

Materials and Methods: Ceramo-metal alloys; Au-Pd, Pd-Ag and Ni-Cr, were cast into 60 dicks (5mm diameter and1.3 mm thickness); 20 samples each. Each alloy samples were divided into four equal groups. They underwent bleaching treatment with 10 % carbamide peroxide for one, two and three weeks. **Results:** For each investigated alloy, its control group had the least corrosion rate and the most corrosion resistance. Au-Pd control group had the lowest rate of corrosion (7.739x10⁻⁶) and the highest corrosion resistance (1.678x10⁶) which gradually impaired as the bleaching time proceeds. Meanwhile, Pd-Ag alloy showed drastic corrosion behavior damage after one week followed by slight decrease after two weeks, then, raised again after three weeks. On the other hand, Ni-Cr alloy control group corrosion behavior was not affected by bleaching agent for one week. Then, the corrosion behavior decreased considerably after two weeks. At the end of third week, the corrosion behavior obviously dropped to the lowest exhibited value in this study.

Similarly, the surface roughness of control groups recorded the least values which increased slightly as the bleaching time proceeded up to three weeks.

Conclusion: 10 % carbamide peroxide has a detrimental corrosive effect on fixed prosthodontics' alloys. This effect becomes obvious with an extended bleaching time. Selecting high nobility alloys and/or stable single-phase microstructures minimize the biological risks.

Key wards: 10 % carbamide peroxide bleaching agent - Prosthodontics alloys – Corrosion resistance - corrosion rate – surface roughness.

INTRODUCTION

Tooth bleaching was reported in the literature as an esthetic treatment option for whitening of intrinsically stained or discoloured teeth. Nightguard vital bleaching technique "home bleaching" with different concentrations of carbamide peroxide is a commonly used as an effective and simple method for bleaching. ^(1,2) It was believed that carbamide peroxide solutions provide their whitening effect through liberation of free radicals. They are very unstable and dissociate into their constituents; 3% to 5% hydrogen peroxide and 7% to 10% urea. Further, the hydrogen peroxide decomposes into oxygen and water, whereas the urea decomposes into ammonia and carbon dioxide. ^(3,4) The extent of treatment for the night-guard vital bleaching technique varies extensively depending on time of application per day in the patient mouth. ⁽⁵⁾

In dentistry, using gold casting alloys is based upon their mechanical properties, biocompatibility and ability to resist corrosion. $^{(6)}$ In the early 1980's, alloys containing more than 75 wt% palladium were introduced to the dental profession as alternatives to gold-based casting alloys. ^(7,8) According to the American Dental Association classification system, ⁽⁹⁾ highpalladium alloys are classified as noble metal rather than high-noble metal because their gold contents range from 0 to less than 10 wt%. The clinical selection of goldbased and high-palladium alloys has decreased in recent years because of the The search for less expensive cost. alternative alloys for fixed prosthodontic restorations has lead to the use of nickelbased alloys with nickel contents of greater than or equal to 50 wt%. These alloys have high strength, modulus of elasticity and (10,11) hardness, adequate ductility and particular casting and: of accuracy importance, their corrosion potentials in the oral cavity.⁽¹²⁾

The chemical attacks of dental alloys in the oral environment known as corrosion. Corrosion not only results in the deterioration and destruction of the restoration but also involves weight loss of materials due to release of ions that is also related directly to the biocompatibility of the alloys. ^(10,13,14) The corrosion properties of alloys depend upon their composition, electrode potentials, stresses and voids on the surface and the surface roughness. ⁽¹⁵⁾ The topographical texture of alloys such surface irregularities make them more prone to corrosion. ⁽¹⁶⁾

The rate at which corrosion takes place is a function of some factors such as the degree of exposure to humidity and temperature, surface condition and types of surface films as well as the nature of corrosion medium. ⁽¹⁷⁾ There are several reports on the effect of bleaching agents on (18) the properties of tooth structure. restorative materials ^(19,20) dental luting agents, ⁽²¹⁾ dental ceramics. ^(1,22) Patients who receive mouth guard bleaching procedures may have metallic restorations such that fixed partial denture. The effects of these bleaching agents on the properties of dental casting alloys that may adversely biocompatibility affect their and/or longevity were not sufficiently available. Therefore, the aim of this study was to examine the effects of a proprietary carbamide peroxide bleaching agent on the corrosion behavior and the surface roughness of different dental casting alloys used in fixed prosthetic dentistry.

MATERIALS AND METHODS

10 % carbamide peroxide Α bleaching product (Opalescence, Ultradent Products Inc, South Jordan, Utah) and three ceramo-metallic alloys were chosen for the study. The elemental compositions of these alloys are listed in table (1). The electrochemical behavior and surface roughness were determined before and after exposure to different bleaching periods.

 Table (1): Type of alloy and elemental composition according to manufacturer

Alloy	Elemental Composition	Manufacturer
Au-Pd	Au: 60.0, Pd: 30.6, In: 8.4, Ga: 1.0, Ru: <1.0 and Re: <1.0	^{IPS} d.SIGN91, Ivoclar, Germany
Pd-Ag	Pd: 57.8%, Ag: 30%, Sn 6% and In 4%	(Pors on 4, Degussa, Germany
Ni-Cr	Ni: 73.7, Cr: 12.6, Mo: 8.0, Al: 3.3, Si: <1.0, Fe: <1.0 and	Pisces, Ivoclar, Germany
	Be: 1.7	-

A total of 60 samples were constructed of the three alloys; 20 samples each. Each alloy samples were divided into four groups; 5 samples were used as a control group and the other three groups underwent bleaching treatment at intervals one, two and three weeks.

Specimen Preparation:

A punch 5 mm in diameter was used in punching base-plate wax sheets to get discs of 5 mm diameter and 1.3 mm thickness. Wax discs of each alloy were sprued. A wetting agent (Surfactant, Delar corp. USA) was directly sprayed on the wax patterns. A universal phosphate investment (FastFire 15, Whip Mix, Lowisville, Kentucky, USA) was used for all alloys. The investment was proportioned and mixed under vacuum (Whip Mix, Lowisville, Kentucky, USA) according to the manufacturer's recommendations. Wax discs were burnt out then casting was performed using a centrifugal casting machine (Kerr, Orange, CA. USA). A separate ceramic crucible was used for each alloy. After casting, the ring was left to bench cool to room temperature. Castings were divested, blasted with 100 µm aluminum oxide particles at 4 bar pressure to remove any residue. The metallic discs were separated from their sprues and air abraded using a 50 µm aluminum oxide particle at 4 bar pressure to finish them. The thickness of the metal discs was adjusted to be 1.3 mm uniform thickness using a digital caliper (Digimatic, Mituotoyo Corporation, Japan). The alloy discs were polished and then steam-jet cleaned. All discs were stored in distilled water in plastic containers at room temperature for 24 hours before any test procedure.

Discs underwent treatment by immersing in the bleaching agent for an average of 8 hours per day. At the end of the bleaching procedure, the treated specimens were removed and washed under running distilled water for 30 seconds and placed in fresh distilled water until the next daily application ^(1,23) The selected intervals assigned for three groups rather than the control one were; one, two and three weeks. Control discs were kept in distilled water that was changed daily.

Corrosion Test:

Prior to testing of the electrochemical characteristics of the different investigated alloys' groups, the surface area of the disc samples exposed to corrosion was calculated.

Electrochemical corrosion tests were carried out using a corrosion measurement system (Autolab PGSTA 30 Potentiostat / Galvanostat, Netherland). Three electrode systems were prepared; saturated calomel electrode (SCE) as reference electrode, auxiliary electrode made of Ag /Ag chloride electrode and the specimen to be tested as a working electrode. These three electrode systems were connected from one side to electrolytic cell that was made of 10 mm beaker glass for potential and polarization measurements. Then, the electrochemical behaviors of these specimens were deduced after immersion in the used bleaching agent as electrolytic media. Finally, the data were plotted automatically through the provided software.



Figure (1): Diagram showing the parts of corrosion system device; (WE) is the working electrode, (RE) is the reference electrode and (CE) is the counter electrode

Electrochemical Measurements:

A controlled potential scan was applied over a small range, typically \pm 25mV with reference to corrosion potential (E_{corr}) at a scan rate of 0.1 mV/s. The slope of the linear polarization curve which is called the polarization resistance (R_P) together with Tafel slopes (β anodic and β cathodic) that were obtained from the Tafel extrapolation were used to calculate the corrosion current density (I_{corr}) and hence the corrosion rate.

Tafel slopes (β cathodic and β anodic) were drawn in the region of linearity of both cathodic and anodic polarization curves on a semi-log plot. The intersection of Tafel slopes determines E_{corr} on vertical abscissa which denotes the ionization tendency of the alloy. The horizontal abscissa, (I_{corr}) is determined indicating the value of the corrosion current density. The increase in the corrosion current density means that the corrosion proceeds. The corrosion current density was calculated using the following formula:

$$I_{corr} = (1/Rp) (ba \ bc/(2.3 \ (ba + bc)))$$

where: ba is the anodic Beta Tafel and bc is the cathodic Beta Tafel

Hence, the corrosion rate (C.R.) could be calculated using the following formula:

$$C.R. = I_{corr} K EW/dA$$

Where: K is a constant that defines the units for the corrosion rate in mm/year.

EW: The equivalent weight in grams/equivalent. d: Density in grams/ cm^3 and A: Area of the sample in cm^2

Surface Roughness Measurements:

Profilometric measurements using a profilometer (Surf Test 402 Analyzer; Mitutoyo Co, Kawasaki, Japan) were carried out for the discs of each alloy. Surface roughness measurements were performed

for the tested groups of each alloy. To measure the roughness profile value of the specimen surface, the diamond stylus was moved across the surface under a constant load of 3.9 mN. The instrument was calibrated using a standard reference specimen, then set to travel at a speed of 0.100 mm/s with a range of 600 mm during testing. Although several surface parameters were recorded. the mean arithmetic roughness (Ra) was used to assess surface changes. Ra is the arithmetic average of the absolute values of the measured profile depth and height of surface irregularities measured from a median line. This procedure was repeated 3 times for all specimens, and the average value was considered to be the mean (Ra) value.



Statistical Analysis:

The data of surface roughness (Ra) was collected, tabulated and statistically analyzed using one way analysis of variance (ANOVA) of SAS program followed by Duncan's test. ⁽²⁴⁾

RESULTS

Electrochemical characteristics:

Table (2) shows the beta anode (ba), beta cathode (bc), corrosion potential (E_{corr}), Corrosion current density (I_{corr}), polarization resistance (Rp) and corrosion rate in

mm/year of all the tested alloys' groups in different selected intervals.

The corrosion resistance values are determined due to the corrosion rate were in commitment but inversely related to the corrosion rate values. Regarding the electrochemical behavior of gold alloy (Aupd), the lowest rate of corrosion (7.739×10^{-6}) and the highest corrosion resistance (1.678×10^6) were recorded by the control group. Gradually, the corrosion rate increased and corrosion resistance decreased as the application time of bleaching proceeds. Meanwhile, the control group of palladium silver alloy (Pd-Ag) showed high resistance (1.829×10^{-5}) corrosion that decreased drastically after one week of

bleaching agent application (3.572×10^{-3}) . After two weeks of bleaching, the corrosion rate was slightly decreased (1.367×10^{-4}) , then, a raised value was recorded after three weeks (4.892×10^{-3}) . On the other hand, control group of nickel chromium alloy (Ni-Cr) revealed corrosion resistance (1.255×10^{-1}) ³) which was not affected by application of bleaching agent for one week (1.492×10^{-3}) . Then, the corrosion rate was decreased considerably on application of bleaching agent for two weeks (5.864×10^{-4}) . At the end of third week of bleaching application, the corrosion rate obviously dropped to the lowest exhibited value (3.071×10^{-2}) in this study.

Table (2): beta anode, beta cathode, corrosion potential, corrosion current density, polarization resistance and corrosion rate of all the tested groups in different selected intervals

Alloy	Sample	ba	bc	E corr	I corr (A/cm ²)	Rp (Ohm)	Corrosion
		V/dec	V/dec	(V)			Rate(mm/y)
bq-nA	Control	0.103	0.245	-0.26	2.317 x10 ⁻⁹	1.678×10^{6}	7.739x10 ⁻⁶
	1 wk	0.098	0.086	-0.247	4.614 x10 ⁻⁹	2.809×10^5	4.972x10 ⁻⁵
	2 wk	0.078	0.325	-0.074	1.728 x10 ⁻⁸	2.262×10^{5}	5.770x10 ⁻⁵
	3 wk	0.257	0.033	-0.23	3.438 x10 ⁻⁷	3.799x10 ³	1.148x10 ⁻³
Pd-Ag	Control	0.068	0.098	-0.295	1.697 x10 ⁻⁹	6.058×10^5	1.829x10 ⁻⁵
	1 wk	0.14	0.076	-0.421	3.315 x10 ⁻⁷	4.915×10^3	3.572x10 ⁻³
	2 wk	0.056	0.093	0.069	1.269 x10 ⁻⁸	6.281x10 ⁴	1.367x10 ⁻⁴
	3 wk	0.246	0.132	-0.476	4.54 x10 ⁻⁷	1.095×10^4	4.892x10 ⁻³
Ni-Cr	Control	0.09	0.178	-0.155	8.666 x10 ⁻⁸	2.827×10^4	1.255x10 ⁻³
	1 wk	0.094	0.061	-0.174	1.03 x10 ⁻⁷	8.567x10 ³	1.492x10 ⁻³
	2 wk	0.057	0.043	0.048	4.049 x10 ⁻⁸	9.361x10 ³	5.864x10 ⁻⁴
	3 wk	0.419	0.136	-0.41	2.121 x10 ⁻⁶	4.115×10^3	3.071x10 ⁻²

Surface Roughness:

Table (3) and figure (3) illustrate the mean and standard deviation of surface roughness of each group within the investigated alloys due to bleaching agent application for the three selected periods one, two and three weeks respectively.

As shown, the control group of Au-Pd alloy recorded the least surface roughness value which increased slightly as the application time of bleaching proceeded up to three weeks. Regarding Pd-Ag alloy, the surface roughness of control group had the lowest value that increased insignificantly after one week but it was significantly higher after two and three weeks respectively. Similarly, the control and one week groups of Ni-Cr alloy were insignificantly different. However, after two weeks, the surface roughness of this group had the highest significant value which was decreased significantly after the third week.

Table (3): The surface roughness (Ra) in µm of the different groups of the investigated alloys for the selected periods

Alloy	Au-Pd	Pd-Ag	Ni-Cr
Group	Mean ± SD	Mean \pm SD	Mean \pm SD
Control	124.519 ± 11.886^{a}	131.401 ±13.750 ^b	131.242 ± 9.555 ^b
1 wk	125.440 ±12.406 a	132.149± 8.134 ^b	$132.668 \pm 7.108^{\text{ b}}$
2 wk	125.480 ± 14.461 ^a	$134.489 \pm 13.213^{\circ}$	135.029 ± 8.771^{d}
3 wk	126.302 ± 9.596^{a}	$134.600 \pm 10.009^{\circ}$	$133.339 \pm 15.045^{\mathrm{c}}$



Figure (3): A Histogram showing surface roughness of the tested groups

DISCUSSION

Corrosion resistance of dental metallic prostheses is an important property; in addition to, other properties such as strength, ductility, and casting accuracy. The galvanic actions due to the intraoral corrosion of casting alloys may cause a series of reactions, including metallic taste, oral burning, oral pain, sensitizations, allergies, and other toxic reactions. ^(25,26) Corrosion behavior of these alloys depends upon their composition, their electrode potentials, surface roughness, and local and (13,15,27) systemic host environment. Theoretically, the corrosion behaviors of alloys can be predetermined by the standard electrode potentials of the alloy elements. ⁽¹⁵⁾ If this standard electrode potential is positive, the metal is regarded as noble that hardly ionizes, whereas if it is negative, the metal is active and ionizes quickly. ⁽²⁸⁾ They are commonly assessed by conventional electrochemical techniques that provide general information about the corrosion susceptibility and resistance, such as the corrosion rate, the range of passivation, and the breakdown potential. (2,29)

The different electrochemical behavior observed with the various investigated dental alloys can be explained by their mechanism of corrosion resistance.

This was achieved through the presence of noble metals or systems and/or formation of passive protective coatings of relatively low corrosion rates. No doubt that noble metals; gold and palladium, have good resistance to corrosion due to low reactivity of the nature of atoms noble. ⁽³⁰⁾ This was documented by the highest corrosion resistance recorded by high noble Au-Pd groups. However, the electrochemical activity of this alloy that composed of (Au: 60.0, Pd: 30.6, In: 8.4, Ga: 1.0, Ru: <1.0 and Re: <1.0) can be explained on the basis of substantial elemental microsegregation within the microstructures of as-cast gold-palladium solid solution matrix ⁽³¹⁾ such a rutheniumrich phase due to the use of ruthenium as a grain-refining element in addition to the other secondary phases. (1,2,7,8,32)

On the other hand, the composition of the investigated Pd-Ag alloy contains 57% pd, %, Ag: 30%, Sn 6% and In 4%. Its corrosion resistance; table (2), might be attributed to the fact that this alloy was found to be highly heterogeneous in its "as-(33) cast" condition. In addition. the commercial Pd-Ag alloys have a lower tarnish resistance due in part to the minor alloying with indium or tin. Moreover, segregation of silver adversely affects both tarnish and corrosion resistance. (2,34) The multiphasic microstructures of Pd-Ag alloys may have some significance for the in vitro and clinical corrosion behavior due to submicroscopic precipitates that remain unaltered even by heat treatment $^{(35)}$ i.e. the metallurgical heterogeneities of these alloys are responsible for the tremendous increase of corrosion. ⁽³⁶⁾ The passivation effect reflected by increasing the corrosion resistance after two weeks may arise from the formation of a surface oxide film, another possibility is enrichment with palladium at the alloy surface as a result of elemental diffusion processes (dealloving). ^(37,38) The selective corrosion that probably

occurs due to the dissolution of less noble elements as (In, Sn, and Ag) and phases because of their lower corrosion potentials than palladium can be passivated at different potentials in an aqueous environment. The passivation of these elements takes place concurrently that would retard or even finally block further corrosion. ⁽³⁹⁾

The corrosion resistance of non noble alloys depends on the integrity of a passivating film. ⁽⁴⁰⁾ The composition of investigated Ni-Cr alloy was (Ni: 73.7, Cr: 12.6, Mo: 8.0, Al: 3.3, Si: <1.0, Fe: <1.0 and Be: 1.7 wt %). Elements such as chromium and aluminum in this alloy have a great affinity for oxygen and thus form a thin passivating oxide film that acts as a protective layer against corrosion. Alloys with chromium in their formulation must contain a minimum of 12% of this element to achieve an adequate passivating film. ⁽³⁰⁾ Molybdenum content does play a significant role in corrosion resistance which exhibit a much wider passivation range and a better resistance to pitting in chloride-containing solutions. ⁽⁴¹⁾ However, the presence of the small amounts of beryllium which are often added to Ni-Cr-Mo dental alloys to improve their castability exhibited non homogenous surface oxide layers and were susceptible to accelerated corrosion. (39,42,43)

During the passivation process, the oxygen concentration and/or pH of the electrolyte often play an important role. It was proven that immersing the alloys in the bleaching agent shifts the equilibrium (44,45) potential to more positive values. There was slight increase in the corrosion resistance of Pd-Ag and Ni-Cr alloys after two weeks of application of bleaching agents extrapolated by positive electrode potentials (Ecorr); table (2). This might be referred to the effect of carbamide peroxide $(CH_6N_2O_3)$ on the corrosion process. The high electron density on nitrogen and oxygen active centers of carbamide peroxide $(CH_6N_2O_3)$ that adsorbed on the metallic surface would form a protective layer isolate it relatively from corrosion medium. It was also reported that the bleaching agents also changed the mechanism of both metallic dissolution and gas reduction. ^(41,46)

The unique and the most relevant property of a casting alloy to its biologic safety is its corrosion. Some elements in the alloy release into the mouth during corrosion. $^{(47)}$ The released cations from the metal surface $^{(10,13,14)}$ might be accompanied by weight loss, that would in turn alter surface textures. Moreover, the surface finish contributes to the corrosion resistance of the dental alloys and influences their electrochemical behaviors, as well. ⁽⁴⁸⁾ It was reported that the surface roughness should be taken into account as an indicator for the tendency towards corrosion. (16,49) The unchanged insignificantly surface roughness (Ra) values of Au-Pd may be attributed to the least electrochemical activities throughout the periods of bleaching agent applications. Meanwhile, the significant increase in surface roughness of Pd-Ag and Ni-Cr alloys after application of the bleaching agent for two and three weeks respectively; table (3), might be referred to passivation. In passivation, a thin film of corrosion products of micrometer thick can form on the surface spontaneously, acting as a barrier against further corrosion. ⁽⁵⁰⁾ This temporarily formed protective layer during the corrosion process is a friable, non uniform porous and loosely attached to substructure and could be subjected to partial or complete disintegration that causing considerable alteration in the surface texture. (39,50)

CONCLUSION

Within the limitations of this study, the following could be concluded:

• A 10 % carbamide peroxide bleaching agent has a detrimental

corrosive effect on Au-Pd, Pd-Ag and Ni-Cr casting alloys.

- This effect becomes obvious with an extended time of bleaching application suggesting more elemental release.
- To minimize biological risks, dentists should select alloys of less corrosive tendency i.e. using high nobility alloys and/or stable singlephase microstructures.
- Practically, the selection of an alloy should be made on a case-by-case basis considering corrosion and biological data from dental manufacturers.

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