Corrosion Behavior of Dental Alloys Under Artificial Saliva Solution with Different pH Values

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Abstract: The purpose of this study was to investigate the corrosion behavior of four different dental casting alloys in artificial saliva solutions with varying pH values. Microstructures were observed using scanning electron microscopy. The corrosion behavior of the experimental alloys in artificial saliva was examined using potentiodynamic polarization measurements. The high noble alloy (Au-8.5Pt-2.6Pd-1.4In) exhibited better corrosion resistance with lower anodic current densities in the pH range of 3–5. The anodic current density of the noble alloy (Au-24.9Pd-19.0Ag-5.5In) decreased as the pH decreased. The noble (Pd-37.7Ag-8.5Sn) and base metal (Ni-25Cr-11.5Mo-1.4Si) alloys exhibited lower corrosion resistance with a relatively high current density at pH 3. Compared with noble alloys, base metal alloys exhibited good corrosion resistance in this study. This makes them a promising material for dental castings considering the complex pH changes in the oral environment.

Keywords: Artificial saliva, Casting alloy, Corrosion resistance.

1. INTRODUCTION

Dental casting alloys are divided into three categories: high noble metals, noble metals, and base metals [1]. High noble metal alloys used for dental casting contain more than 75% precious metal elements (gold, palladium, and platinum). The noble metal alloy composition contains 25%–75% precious metal (low-gold, Pd-Ag alloy) and is mainly composed of gold, silver, copper, and a small amount of palladium. These metals are often used in dental prosthetics such as dental crowns. Gold alloys are some of the most common noble metals, having good biocompatibility, corrosion resistance, and mechanical properties. However, many metals can replace gold alloys in clinical applications, such as noble metals (Ag-Pd alloys), base metals (Ni-Cr, Co-Cr, or Co-Cr-Mo alloys), and titanium alloys. The choice of dental prosthetic materials also varies according to many considerations, in particular the price. These replacement alloys exhibit good mechanical properties while being inexpensive.

Population aging causes the requirement of dental prosthetics at different points of time, and it is common to have more than one metal denture in the oral environment. In previous studies, patients have reported pain due to the simultaneous contact of two metals or the same electrolyte, with symptoms such as pain and discomfort in the tongue, disturbance in taste or smell, and oral mucosal pain. More severe symptoms include emesis, vertigo, cephalgia, and neuralgic pain [2]. This phenomenon is known as oral galvanism (OG). Thus far, OG has been considered to be a result of the flow of ions or the "battery effect" of metallic restorations. Different dental metals have different potentials for this phenomenon. Because of the larger potential difference, the flow of ions is more likely to be contained in the electrolyte (oral fluids); this flow produces a spontaneous reaction.

Furthermore, the oral environment changes frequently because of the different eating habits of each individual. Thus when dental metal is placed in the mouth, it must withstand environmental pH changes. Taher and Al Jabab [3] investigated the Cavani corrosion between implants and crowns in artificial saliva with a pH of 7.2 and reported that Ni-Cr alloys and titanium alloys produced relatively unstable

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galvanic corrosion. Therefore, this study used electrochemical experiments to measure the potential difference between the corrosion phenomena of dental alloys and titanium alloys in artificial saliva with different pH values.

2. MATERIALS AND METHODS

2.1. Materials

Four commercially available dental alloys routinely used for metal–ceramic restorations were evaluated. According to the classification standard of the American Dental Association (ADA), dental casting alloys are selected and classified as high noble, noble, and base metal alloys. The compositions of the alloys, as determined by the manufacturer, are provided in Table **1**.

2.2. Microstructure Observation

The disc specimens were ground with SiC abrasive paper up to grade #2000 and polished with 0.3 μm Al_2O_3 powder to ensure that the surface roughness reached at least Ra < 0.2 μm. The specimens (n=3 in each group) were etched using an ethanol solution containing 25% HNO_3 and 15% HCl. The microstructure of the alloys was observed using a scanning electron microscope (SEM, JEOL, JSM-6380, Japan) with a working voltage of 15 kV, and the representative findings were selected for analysis.

2.3. Electrochemical Test

Corrosion tests were performed in an artificial saliva solution (400 mg/L KCl, 400 mg/L NaCl, 780 mg/L $NaH_2PO_4 \cdot 2H_2O$, 795 mg/L $CaCl_2 \cdot 2H_2O$, 5 mg/L $Na_2S \cdot 9H_2O$, and 1000 mg/L urea). The pH of the test solutions was adjusted to 3.0, 4.0, 5.0, and 6.0 by adding HCl. An Ag/AgCl reference electrode and platinum counter electrode were used for the corrosion tests. A chemical analyzer (CHI614D, CH Instrument, USA) was used to perform potentiodynamic polarization and corrosion potential tests. The test temperature was maintained at 37 °C and the scan rate was 1 mV/s. Corrosion parameters, including the corrosion potential (E_{corr}) and corrosion current density (I_{corr}) obtained from the potentiodynamic polarization curves, were used to evaluate the corrosion resistance of the alloys. For the potentiodynamic polarization test, the specimens were immersed in the electrolyte without any impressed potential for 1 h to stabilize the passive film prior to the measurement.

3. RESULTS

3.1. Microstructure

Figure **1**(**a**) shows that the basic structure of the HG alloy was a dual-phase structure with some precipitates, and no obvious grain boundaries could be observed, indicating that its grain size was large. It was also observed as a casting structure (including casting shrinkage holes) as there were casting segregation features and precipitates, and the precipitates had the characteristics of directional consistency. The microstructure of the LG alloy was similar to that of the high-gold alloy, which had a single-phase equiaxed crystal structure. In addition, the grain boundaries can be observed in Figure **1**(**b**). Furthermore, there were obvious casting shrinkage cavities and square holes similar to precipitates found in the base in the LG alloy.

Two different phases could be clearly seen in the microstructure of the PA alloy, indicating that the PA alloy had a duplex phase microstructure [Figure **1**(**c**)]. In addition, the PA alloy had relatively few casting defects, and precipitates were also observed. The NC alloy had a typical dendritic structure and obvious casting segregation, as shown in Figure **1**(**d**). The NC alloy was single-phase and accompanied by precipitates.

Table 1: Chemical Compositions of the Four Commercially Available Dental Casting Alloys (HG, LG, PA, and NC alloys)

Type	Materials	Manufacturer	Composition (Mass %)	Others
High noble	AH (high gold, HG)	WORLD, USA	Au-8.5% Pt-2.6% Pd-1.4% In	Ir<1.0% Fe<1.0% Ta<1.0%
Noble	ARGEDENT 500 (low gold, LG)	Argen, USA	Au-Pd 24.9% - Ag-19.0%-In 5.5%	Ir<1.0%, Ga<1.0%
Noble	W-1 (palladium-silver, PA)	Ivoclar Vivadent, USA	Pd-Ag 37.7% -Sn 8.5%	In<1.0% Ru<1.0% and Li<1.0%
Base metal	KN (nickel-chromium, NC)	System, USA	Ni-Cr 25%-Mo 11.5% -Si 1.4%	-

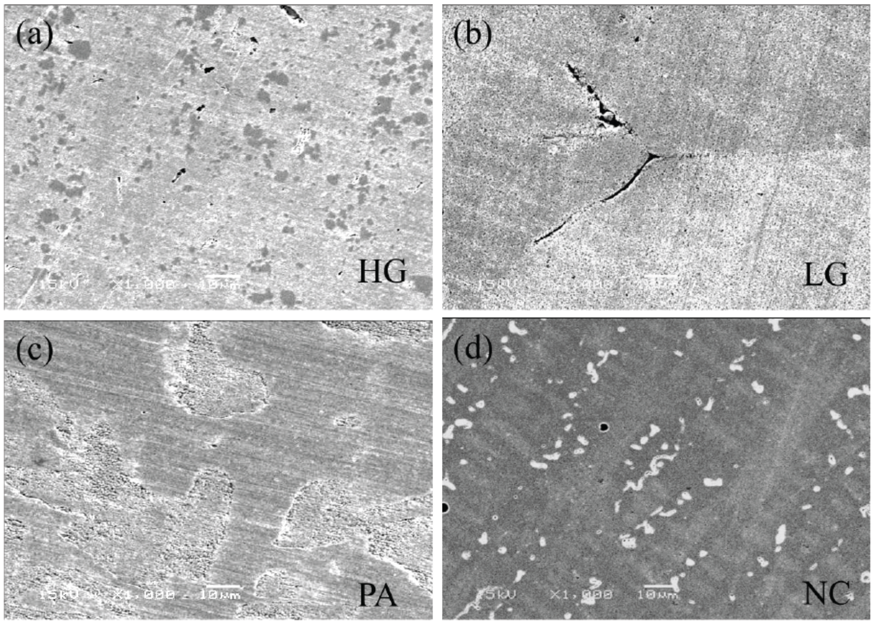

Figure 1: Scanning electron microscopy findings for the four commercially available dental casting alloys (**a**) HG, (**b**) LG, (**c**) PA, (**d**) NC.

3.2. Electrochemical Behavior

The polarization curves and corrosion parameters of the HG, LG, PA, and NC alloys in artificial saliva are shown in Figure **2**(**a**) and Table **2**, respectively. The corrosion potentials (E_{corr}) of HG, LG, PA, and NC under artificial saliva (pH=7) were -0.048, -0.177, -0.046, and -0.378, respectively. HG and PA alloys had a higher corrosion potential in this environment. The corrosion potential is considered to be the driving force of the reaction, indicating that the material requires more energy to undergo a polarization reaction. In addition, the corrosion current density (I_{corr}) values of HG, LG, PA, and NC alloys under artificial saliva (pH=7) were 2.5, 6.1, 0.2, and 0.1 10^{-8}A/cm^2, respectively. The lower current density and highest corrosion potential of the PA alloy under artificial saliva (pH=7) indicated that the material exhibited a higher corrosion resistance.

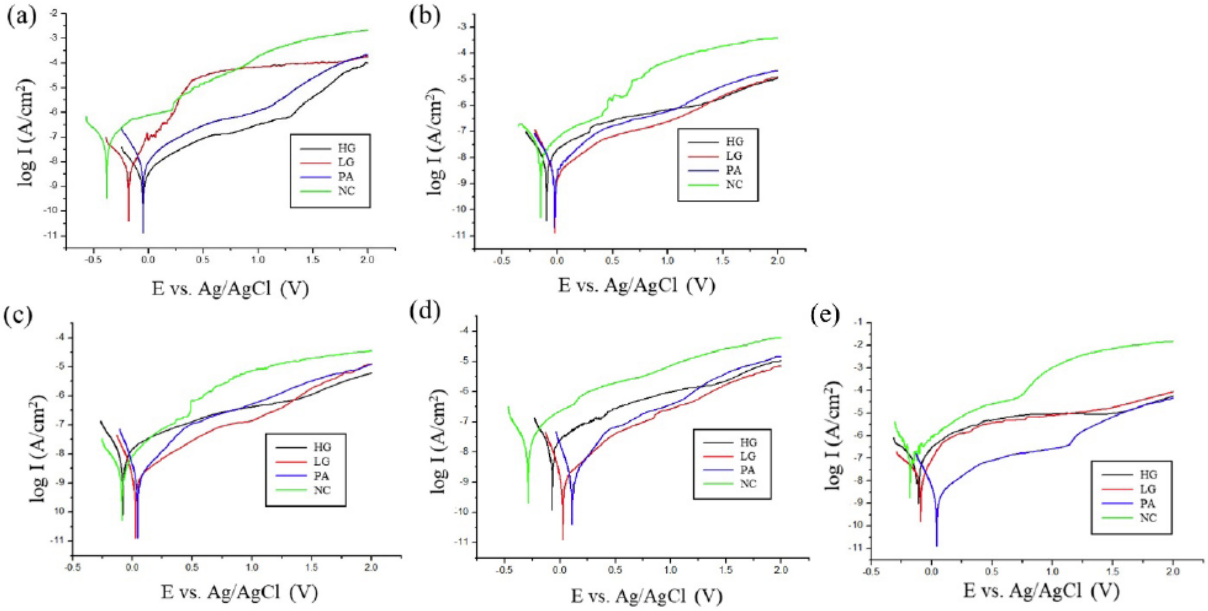

Figure 2: Potentiodynamic polarization behaviors of HG, LG, PA, and NC alloys in artificial saliva solutions (**a**) pH=7, (**b**) pH=6, (**c**) pH=5, (**d**) pH=4, (**e**) pH=3.

Table 2: Corrosion Parameters [E_{corr}(V) and I_{corr}(10^{-8}A/cm^2)] for Casting Alloys in an Artificial Saliva Dynamic Polarization Test

Material	pH=7		pH=6		pH=5		pH=4		pH=3	
	E_{corr}	I_{corr}	E_{corr}	I_{corr}	E_{corr}	I_{corr}	E_{corr}	I_{corr}	E_{corr}	I_{corr}
HG	-0.048	2.5	-0.099	8.4	-0.078	0.1	-0.068	0.2	-0.106	0.4
LG	-0.177	6.1	-0.019	2.9	0.027	2.0	0.029	1.9	-0.088	0.1
PA	-0.046	0.2	-0.027	4.7	0.047	2.1	0.112	1.9	0.045	2.5
NC	-0.378	0.1	-0.150	0.2	-0.084	1.3	-0.286	0.1	-0.154	2.4

The corrosion potentials (E_{corr}) of HG, LG, PA, and NC under artificial saliva (pH= 6) were -0.099, -0.019, -0.027, and -0.150 V, respectively [Figure **2**(**b**)]. LG alloys had higher corrosion potentials, similar to those of PA alloys. In contrast, the corrosion potentials of HG alloys tended to decrease. However, the corrosion potentials of nickel-chromium alloys were similar to those of high-gold alloys in artificial saliva (pH=6). A comparison of the corrosion currents revealed that those of alloys containing precious metal components exhibited an upward trend, whereas the corrosion currents of the NC alloys remained the same. Overall, compared with a pH of 7, the corrosion potential of each alloy exhibited an upward trend. The current density (I_{corr}) of HG, LG, PA, and NC alloys under artificial saliva (pH=6) were 8.4, 2.9, 4.7, and 0.2 10^{-8}A/cm^2, respectively. The NC alloy had better corrosion characteristics than other alloys in artificial saliva with a pH of 6.

The polarization curves of the alloy when the pH of the artificial saliva decreased to 5 are shown in Figure **2**(**c**). The corrosion potentials of the HG, LG, PA, and NC alloys in artificial saliva (pH=5) were -0.078, 0.027, 0.047, and -0.084 V, respectively. The PA alloy had the highest corrosion potential; however, the corrosion potential value of the LG alloy was higher than that of artificial saliva at a pH of 7, showing that the LG alloy required more energy to cause it to begin to corrode at a pH of 5. The corrosion potentials of HG, LG, PA, and NC alloys under artificial saliva (pH=5) were 0.1, 2.0, 2.1, and 1.3 10^{-8}A/cm^2, respectively. Overall, both the corrosion potential and current had better corrosion characteristics in this environment than at a pH of 7 and 6, and the PA alloy had the highest corrosion potential at a pH of 5.

The corrosion potentials of the HG, LG, PA, and NC alloys in artificial saliva (pH= 4) were -0.068, 0.029, 0.112, and -0.286 (V), respectively. The corrosion potential of the PA alloy was much higher than that of other alloys and was also higher than that at a pH of 7. The corrosion potentials of the HG, LG, PA, and NC alloys in artificial saliva (pH=4) were 0.2, 1.9, 1.9, and 0.1 10^{-8}A/cm^2. Figure **2**(**e**) and Table **2** show the polarization curves and corrosion parameters of the alloys in solution at the most acidic artificial saliva (pH=3), respectively. The corrosion potentials of HG, LG, PA, and NC alloys were -0.106, -0.088, 0.045, and -0.154 V and the corrosion currents were 0.4, 0.1, 2.5, and 2.4 10^{-8}A/cm^2, respectively. The PA alloy had the highest corrosion potential, but there was no obvious difference between the HG and LG alloys. In the NC alloy, the corrosion current exhibited an upward trend with decreasing pH to 3, indicating that the corrosion resistance of the NC alloy in acidic artificial saliva was lower than that of other precious metal alloys.

4. DISCUSSION

Alterations in types of dental alloy casting systems led to a change in corrosion behavior in this study. The oral environment may present aggressive conditions, particularly in acidic artificial saliva at pH 3–6, and the stability of the alloy is greatly reduced under these conditions. In terms of corrosion characteristics, traditional belief is that the higher the gold content, the better the corrosion resistance. However, in this study, the corrosion potential of the HG alloy containing 85% gold was in the range of -0.106 to -0.098 V at pH values of 3–6. Furthermore, the corrosion potential was worse than that of the LG alloy (-0.088 to 0.029 V) containing 50% Au. In this study, some precipitates were observed in the HG alloy, as shown in Figure **2**, and the precipitates tended to be concentrated. This indicates the problem of casting segregation during the casting process. In LG alloys, some small precipitates can be found in the grains, and defects caused by casting may also be observed.

The corrosion process of dental metals takes place under a complex system, and many factors must be considered such as alloy composition, microstructure, manufacturing method, and external environmental factors (temperature and pH). In other studies, it has been posited that the composition and microstructure of the material composition have a greater influence on corrosion behavior. Li *et al*. [4] proposed that single-phase alloys are more resistant to corrosion than multiphase alloys because they do not exhibit galvanic corrosion effects. These elements produce synergistic effects that increase or decrease the corrosion behavior and characteristics of the alloy.

Yang *et al*. [5] suggested that the anode and cathode of the alloy exist uniformly over the entire corroded surface in solid-solution (single-phase) alloys. In this case, because corrosion products were continuously released anywhere on the surface of the metal, it should have been unfavorable for corrosion products to deposit on the alloy surface to form a passivation layer. However, in the structure of the multiphase alloy, the anode and cathode of the alloy are separated, most likely because the two elements have different corrosion potentials, and a large amount of galvanic corrosion occurs on the surface of the alloy itself. In this case, if an element with a lower medium potential in the alloy is used as the anode and an element with a higher potential is used as the cathode, the corrosion products can be concentrated on the element phase with a higher potential to form a stable surface. Because the material composition of the LG alloy in this study was more diverse than that of the HG alloy, it produced tiny galvanic corrosion effects. Therefore, a passivation layer can be formed on the surface under different pH environments to reduce the corrosion rate.

As shown in Figure **1**, this study showed that the PA has a duplex-phase microstructure, and some small precipitates could be observed in the PA alloy after casting and cooling. The microstructure of the palladium-silver alloy in this study was similar to that of Viennot *et al*. [6], as shown in Figure **1**(**c**), and it is believed that the brighter regions on the grain boundaries are in the palladium-rich phase. Regarding the influence of the casting method, Sarantopoulos *et al*. has studied the optimization of the palladium-based alloy casting process, and it is believed that the casting temperature has a significant influence on palladium-based alloys. This can easily affect the microstructure after alloying [7]. In addition, other researchers have pointed out that carbon can easily cause surface pores to form on the surface of high palladium alloys, but it has no effect on the corrosion resistance of the material [8]. In this study, the corrosion potential of the PA alloy in a more acidic environment (pH=3-5) was between 0.045 and 0.112 V, which was higher than those of the other three alloys.

The similar corrosion resistance of palladium-silver alloys and high-palladium alloys is attributed to the composition of their alloys [9]. Although the palladium content of PA alloys is only approximately 50 wt%, they still have a similar corrosion resistance under different pH values. Base elements such as silver and tin form an additional passivation layer on the surface, which could further improve the corrosion resistance of the palladium-silver alloy. Most base metal alloys, such as Co-Cr alloys and Ni-Cr, have inherently dendritic cast structures with more complex phase structures. These phase structures are mainly affected by the addition of alloying elements, which induce the formation of precipitates or the appearance of secondary phases [10]. The concentration of Cr in the base metal has a key influence on the passivation layer of the material. Although the overall alloy system has a greater impact, for the base metal, the content of chromium element is greater than 12 wt% for the passivation layer of the overall alloy to obtain proper stability [11]. The poor stability of the base metal itself to the passivation layer and the occurrence of casting segregation result in excessive concentration or dispersion of elements in specific areas of the microstructure. This makes the base metal prone to pitting in specific areas, resulting in unstable corrosion-resistance properties.

5. CONCLUSION

The results of this study suggest that the presence of higher Au (75 mass%) in the bulk alloy does not lead to superior corrosion resistance compared with that of some noble or base metals in acidic artificial saliva at pH 3–6. Moreover, the addition of Ag and Sn to form an additional passivation layer on the surface can further improve the corrosion resistance of the alloy.

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