Original Article Influence of four heat treatments on the corrosion resistance of magnetic attachment keepers

Wenqi Hu, Yijun Wang, Zexin Gan

Shanghai Huangpu District Dental Clinic, Shanghai 200001, China

Received March 21, 2016; Accepted September 7, 2016; Epub October 15, 2016; Published October 30, 2016

Abstract: Magnetic attachment keepers used in dental implants are treated in one of the following ways: Co-Cr alloy casting, Ni-Cr alloy casting, gold alloy casting, and laser welding (Ni-Cr alloy). All four treatments can partially change the surface structure of the magnetic attachment keepers and affect the keepers' resistance to corrosion. The objective of this study was to evaluate the differences in the corrosion properties of magnetic attachment keepers processed using the four treatments and tested in artificial saliva. Magnetic attachment keepers were treated with Ni-Cr metal ceramic alloy, Co-Cr alloy, and gold noble metal alloy and welded by spot laser, forming samples to be immersed in artificial saliva and tested 10 and 20 days after treatments. An inductively coupled spectrum instrument was used to detect the ionic (Fe, Cr, and Mo) concentrations in the soaking solution. Co-Cr, Ni-Cr, and gold alloy treatments showed the largest amounts of precipitated Fe and Mo ions in artificial saliva (all *P*<0.05 vs. the control and laser treatments, except for Mo ions in Gold alloy vs. laser 10 days after treatments, and Ni-Cr vs. control, Ni-Cr vs. laser, Gold alloy vs. laser 20 days after treatments). Co-Cr treatment showed the largest amount of precipitated Treatments, and Ni-Cr vs. control, Ni-Cr alloy casting, gold alloy casting, and laser welding could decrease the keepers' resistance to corrosion in the oral environment. Laser welding showed the least decrease in corrosion resistance of the keepers.

Keywords: Magnetic attachment, keeper, corrosion resistance

Introduction

A magnetic attachment is a device used in dentistry that uses a magnetic force to ensure that a restoration device adheres to a dental abutment or implant for fixation and stabilization. The magnetic attachment is composed of a permanent magnet installed at the tissue surface of the denture and a magnetized soft alloy (keeper) placed in the intraoral remaining dental root surface, proximal to the abutment or implant. The axial retention of the attachment is strong and persistent, and antagonizes lateral and twisting forces by shifting or even dislocating, which can protect the abutment. In addition, the device has other advantages such as an unrestricted insertion direction, an automatic reset, and lack of a visible clasp for aesthetic value; therefore, it is becoming more and more popular with dentists and patients [1].

The keeper is formed mainly by cold forging or cold working, and its primary structure is single-phase ferrite compound (Fe-19Cr-2Mo) with a uniform and dense metallic structure. The end product keeper must be connected to dental metal to form the root surface cap, which is achieved using one of the four following treatments: Co-Cr alloy casting, Ni-Cr alloy casting, gold alloy casting, or laser welding. The three alloy treatments use the cast-bonding method by which the end product keeper is an investment cast with the root cap forming an integral whole. A noble metal such as gold, mixed with another metal to create a gold alloy with a low melting point, is commonly used for the root cap in many countries; however, in China, lessexpensive base metals such as Co, Cr, and Ni are often used to create various alloys used for the root cap. Laser welding is a method that has been developed over the years and that integrates the keeper with the pedestal by accurately controlling the welding zone with a laser [2].

The keeper that is processed by heating dental metal often shows different levels of corrosion,

after 10 days in artificial saliva					
Group	Fe	Cr	Мо		
Co-Cr	247.80±38.40 ^{*,#}	3.32±1.37 ^{*,#}	283.20±25.82*,#		
Ni-Cr	173.30±40.30 ^{*,#}	0.19±0.27	31.00±10.86 ^{*,#}		
Gold alloy	361.80±65.84 ^{*,#}	0	22.60±4.55*		
Laser	13.30±1.95	0	12.40±1.84		
Control	0	0	0		
P^{Δ}	< 0.001	< 0.001	< 0.001		

Table 1. Concentrations of metal ions from keepersafter 10 days in artificial saliva

Data are shown as mean \pm standard deviation (n=10/group). *P<0.05 vs. the control group; #P<0.05 vs. the laser group. Δ : Overall P values among five groups (ANOVA).

such as tarnishing, rust, desquamation, and fracture, affecting the working life of the magnetic retainer. In addition, precipitation (leaching) of some metal ions poses a potential danger of toxicity to the patients [3, 4].

Therefore, the present study aimed to assess qualitatively and quantitatively the changes in corrosion resistance of keepers after dental metals were heat treated and exposed to artificial saliva. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to measure the precipitated metal ions. This method uses ICP as the excitation source to study the emission spectrum of the atom and has several advantages such as being highly accurate, having stability without interference, and having the ability to detect multiple elements at the same time or in order. ICP-AES is an effective method to detect multiple trace elements in solution.

Materials and methods

Materials and instruments

The AUM20 keepers were purchased from Aichi Steel (Tokai, Japan), the Ni-Cr ceramic alloy and gold noble metal were from Heraeus Kulzer (Hanau, Germany), and the Co-Cr alloy was from Dental Materials Plant in Shanghai (China). The HT-W120 laser spot welder was purchased from Shenzhen Chinasky Laser Technology Co, Ltd. (Shenzhen, China), the CS501-3C thermostatic water bath was from Chongqing Sida Experimental Equipment Co., Ltd. (Chongqing, China), and the ICP-MS ICPE9000 was from SHIMADZU Corporation (Kyoto, Japan).

Sample preparation

Fifty AUM20 keepers were divided into five groups (n=10/group). Three groups were pro-

cessed by conventional investment casting, grinding, and buffing with Ni-Cr ceramic alloy, Co-Cr alloy, and gold noble metal alloy, respectively. The fourth group was polished by laser spot welding before welding using a pedestal welder. The keepers were welded onto the cast dowel-copings made from Co-Cr alloy using a Nd: YAG laser spot-welding apparatus. All samples were in sheet form measuring 8.0 mm in diameter and 3.0 mm thick, and were sealed and fixed with epoxy resin, exposing only the test sur-

face (i.e., the surface in contact with the magnet). The fifth group was the control group and was sealed and fixed directly with epoxy resin, exposing the test surface. All samples were cleaned with ultrasound for 10 min with acetone and ethanol.

Corrosive medium

The corrosive medium was artificial saliva using ISO/TR10271 as the standard. The components were: 0.4 g·L⁻¹ NaCl, 0.4 g·L⁻¹ KCl, 0.78 g·L⁻¹ Na_2HPO₄·2H₂O, 0.795 g·L⁻¹ CaCl₂·2H₂O, 0.005 g·L⁻¹ Na_2S·2H₂O, and 1.0 g·L⁻¹ urea. Analytical grade reagents and distilled water were used, and NaOH and HCl were used to adjust the pH to 7.0. All experiments were performed at 37± 1.0°C [5, 6].

Immersion test

The samples in the control and study groups were completely immersed into sealed tubes containing 20 mL artificial saliva and placed in a thermostatic water bath at 37°C. Five milliliters of the suspension was removed on days 10 and 20 to measure the precipitated amounts of Fe, Cr, and Mo. The concentrations of metal ions in the test solution of each group were determined using the standard curve created by ICP-mass spectrometry (-MS).

Statistical analyses

Data were analyzed using SPSS 10.0 for Windows (SPSS Inc., Chicago, IL, USA). Data were shown as means \pm standard deviation (SD) and analyzed using one-way analysis of variance (ANOVA) with the Dunnett's post hoc test. Differences were considered significant at a *P*-value of <0.05.

Table 2. Concentrations of metal ions from keepers after
20 days in artificial saliva

Group	Fe	Cr	Мо
Co-Cr	721.20±123.48 ^{*,#}	10.12±4.62 ^{*,#}	519.20±92.70*,#
Ni-Cr	645.80±58.30 ^{*,#}	0.65±0.48	43.30±12.43
Gold alloy	681.40±123.34 ^{*,#}	0	60.00±15.00*
Laser	10.00±2.21	0	15.40±3.86
Control	0	0	0
P^{Δ}	<0.001	<0.001	<0.001

Data are shown as mean \pm standard deviation (n=10/group). *P<0.05 vs. the control group; #P<0.05 vs. the laser group. Δ : Overall P values among five groups (ANOVA).

Results

Tables 1 and 2 present the concentrations of metal ions from keepers after 10 and 20 days in artificial saliva, respectively. The control keepers did not release any detectable amount of metal ions. Co-Cr, Ni-Cr, and gold alloy treatments showed the largest amounts of precipitated Fe ion in artificial saliva (all P<0.05 vs. the control and laser treatments). Co-Cr, Ni-Cr, and gold alloy treatments also showed the largest amounts of precipitated Mo ion in artificial saliva (all P<0.05 vs. the control and laser treatments, except for Gold alloy vs. laser after 10 days in artificial saliva, and Ni-Cr vs. control, Ni-Cr vs. laser, Gold alloy vs. laser after 20 days in artificial saliva). Furthermore, Co-Cr treatment showed the largest amount of precipitated Cr ion in artificial saliva (all P<0.05 vs. the control and laser treatments).

Discussion

Ferritic stainless steel is the alloy commonly used in dentistry to make magnetic keepers. This alloy is constantly exposed to the warm and humid environment of the mouth and is affected by mastication, saliva containing electrolytes, and a complicated microbial community, all of which leading to various levels of corrosion such as tarnishing, rust, desquamation, and fracture. As a result of being completely and constantly immersed in saliva, metal ions will precipitate from the keepers, causing a detrimental effect on adjacent tissues. In addition, because of the different components and metallographic phases of alloys, the type and amount of the precipitated metal ions vary, also causing different effects on adjacent tissues. The more ions that precipitate, the less resistance of the keeper to corrosion and the higher the toxicity to the patient [7]. Because of the various metal-binding processes, when several metals are intermixed the metals' resistance to corrosion will be further compromised, increasing the possibility of galvanic corrosion. The durability and safety of the commonly used keepers must be considered because they will be used in the oral environment for a long time.

Metal corrosion is the damage to metal caused by chemical and electrochemical reactions with the metal's surroundings, which often occur at the metal-medium interface. Alloy metals are used in most dental restorations, and their long-term exposure to the oral environment leads to different levels of corrosion. Corrosion can cause the release of metal ions into the local oral tissues, resulting in inflammation of the gingival and periodontal tissues. The keeper in the magnetic attachment cast is fixed in the root canal of the teeth, exposing its surface to the oral environment. After some time, surface staining and roughness increase and magnetic attraction decreases, which are considered by some authors to be associated with corrosion [8].

In a previous study, we detected metal corrosion using a "weight-loss" method that was converted into a corrosion rate, but the accuracy of the method was low. Here, we used ICP-MS, a highly sensible and accurate method, to detect the precipitated metal ions in artificial saliva for each alloy sample, and further analyzed the influences of the metal-binding process on the keepers' corrosion resistance. This method has several advantages, such as strong selectivity, low detection threshold, high accuracy, and quick analysis [9, 10]. Using this method, the precipitated metal ions could be detected in each study group but in highly different amounts. The results showed that the precipitated amounts of metal ions when using the Co-Cr alloy, Ni-Cr alloy, or gold alloy were significantly higher than those in the control group, suggesting that these casting methods decreased the corrosion resistance of the magnetic attachment keeper material. The precipitated amount of metal ions from the sample

processed by laser welding was higher than that of the control group, which indicated that laser welding could also decrease the corrosion resistance of keeper metals, but the amount was far lower than that in the other three alloy groups, suggesting that laser welding is much less destructive on keeper metals (**Tables 1** and **2**).

The high temperature during casting destroys the original metallurgical structure of the keeper, changing the single-phase structure into a multiple-metal structure and polycrystalline phase structure mixed with ferrite, austenite, and martensite. The formed crystalline grain with a non-uniform size easily causes intergranular corrosion [11] and forms either a rugged oxide layer on the surface or surface indentation from the collapse of the crystalline grains. In this case, a polishing process is needed, which will change the smoothness of the original surface [12, 13] and decrease the magnetic adsorption and corrosion resistance to a value that is significantly lower than that of the original end product keeper. In addition, by using the conventional polishing process, the surface smoothness of the end product keeper cannot be achieved; therefore, its resistance to corrosion is lower. Because laser welding do not destroy the main part of the keeper, forming only a melting region of about 0.25-0.30 mm in width at the junction zone, this method did not change the metallurgical structure. The center of the keeper was still a large ferrite crystal and although the surface smoothness was not as good as that of the original end product keeper after polishing, it was still better than that of the cast keepers [14]; therefore, the corrosion resistance of the laser welded keepers was higher than that of cast keepers.

The processing technology for the magnetic attachment keepers, using Co-Cr alloy, Ni-Cr alloy, gold alloy, or laser welding, increased the precipitation of metal ions from the keepers in artificial saliva, suggesting that the processing methods for casting and laser welding could destroy the keepers' resistance to corrosion. Our results showed that the value of the metal ions in the laser welding group was far lower than that in the other groups. This suggested that the laser welding process was a better method by which to preserve the keepers' resistance to corrosion in the mouth. Corrosion resistance of the magnetic attachment keepers is one of the most important indices for evaluating biocompatibility; therefore, determining the best keeper materials, root cap alloys, and processing technology could improve the keepers' corrosion resistance.

The present study is limited and focused mainly on the keeper materials and not on conditions such as the size of the keepers, surface area ratio of the embedded keepers and other metals, and surface roughness of the specimens. In addition, the keepers that must be cast or welded by laser can be used in clinical settings. The oral environment is far more complicated than the environment obtained using artificial saliva and an incubator, and cannot be duplicated in the laboratory; therefore, these factors need further study and exploration.

Disclosure of conflict of interest

None.

Address correspondence to: Wenqi Hu, Shanghai Huangpu District Dental Clinic, Shanghai 200001, China. Tel: +86-13022115799; Fax: +86-21-6321-5792; E-mail: 13022115799@163.com

References

- Boeckler AF, Morton D, Ehring C and Setz JM. Mechanical properties of magnetic attachments for removable prostheses on teeth and implants. J Prosthodont 2008; 17: 608-615.
- [2] Du L, Zhong HL and Lin C. Experimental study of laser welding technology to improve welding quality on the armature. J Clin Stomatology (In Chinese) 2008; 24: 149-152.
- [3] Boeckler AF, Ehring C, Morton D, Geis-Gerstorfer J and Setz JM. Corrosion of dental magnet attachments for removable prostheses on teeth and implants. J Prosthodont 2009; 18: 301-308.
- [4] A P, S M and MC M. Corrosion behaviour of silicon-carbide-particle reinforced AZ92 magnesium alloy. Corrosion Sci 2009; 51: 841-849.
- [5] Cao YL, Zhu S and Liu H. Mensuration of corrosion potential of dental restorative alloys in common use. Journal of Modern Stomatology (In Chinese) 2006; 20: 308-309.
- [6] Dong H, Nagamatsu Y, Chen KK, Tajima K, Kakigawa H, Shi S and Kozono Y. Corrosion behavior of dental alloys in various types of electrolyzed water. Dent Mater J 2003; 22: 482-493.
- [7] Wylie CM, Davenport AJ, Cooper PR and Shelton RM. Oral keratinocyte responses to nickel-

based dental casting alloys in vitro. J Biomater Appl 2010; 25: 251-267.

- [8] Zhao J, Wei B and Li Y. [Comparison of the difference of the magnetic force by cast postkeepers combined with three different metals]. Shanghai Kou Qiang Yi Xue 2006; 15: 431-433.
- [9] Joska L, Poddana M and Leitner J. Corrosion behavior of palladium-silver-copper alloys in model saliva. Dent Mater 2008; 24: 1009-1016.
- [10] van Vuuren LJ, Odendaal JS and Pistorius PC. Galvanic corrosion of dental cobalt-chromium alloys and dental amalgam in artificial saliva. SADJ 2008; 63: 034-038.
- [11] C G, F M and P DT. Pitting corrosion of welded joints of austenitic stainless steels studied by using an electrochemical minicell. Corrosion Sci 2008; 50: 1184-1194.

- [12] Pow EH, Chan KH, Luk HW, Dias AP and McMillan AS. Effect of burn-out temperature on magnetic keepers in cast noble metal alloy posts. J Prosthet Dent 2009; 101: 66-72.
- [13] Zheng YL, Wei B and Yao H. The study of metallurgical structure changes before and after the armature with metallic cast. J Shanghai Stomatology (In Chinese) 2006; 15: 416.
- [14] Chao Y, Du L and Yang L. Comparative study of the surface characteristics, microstructure, and magnetic retentive forces of laser-welded dowel-keepers and cast dowel-keepers for use with magnetic attachments. J Prosthet Dent 2005; 93: 473-477.