



Effect of hydrogen peroxide concentration on surface properties of Ni–Cr alloys



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Received 9 April 2015; accepted 3 March 2016

Abstract: The effect of concentration of hydrogen peroxide (H_2O_2) on the surface properties of Ni–Cr alloys was studied. Surface roughness and surface morphology of Ni–Cr alloys were evaluated by surface profiler and scanning electron microscopy after being immersed in different concentrations of H_2O_2 for 112 h. Surface corrosion products of Ni–Cr alloys were analyzed by photoelectron spectrograph after being immersed in 0% and 30% H_2O_2 . The order of increasing surface roughness of Ni–Cr alloys after being immersed in different concentrations of H_2O_2 was $0 < 3.6\% < 10\% < 30\%$. As the concentration of hydrogen peroxide increased, the surface roughness of Ni–Cr alloys increased and the surface morphology showed different degrees of corrosion. According to the XPS results, the corrosion products formed on the outmost surface layer of the studied samples are $Ni(OH)_2$ and BeO.

Key words: hydrogen peroxide (H_2O_2); dental Ni–Cr alloys; surface roughness; surface morphology; surface corrosion products

1 Introduction

With the development of oral repair techniques, porcelain fused-to-metal prosthesis is approved by patients because of its strength of metal and beautiful outlook of porcelain. For clinical dental applications, there are currently hundreds of alloys available for prosthodontic restorations. Among them, nickel-based (Ni–Cr) alloy prosthesis is widely used (especially in developing countries) in the inner crown of casting crown and bridge and porcelain-fused-to-metal crown and bridge owing to its simple fabrication process, low cost, and additionally, improvement of castability and oxidizability. However, the oxidizability increment is accompanied by an increment of the corrosion rate, which has the disadvantage to release nickel (which presents an allergen character) and chromium (able to be present as toxic chromate) in the human system. Nickel might activate monocytes and endothelial cells, suppressing or promoting the expression of intercellular adhesion molecule-1 (ICAM-1) by endothelial cells, depending on the ionic concentration [1].

Although Ni–Cr alloys are well-known for their good corrosion resistance in the body, the metal surface exposed to oral cavity rich in electrolytes would generate electrochemical corrosion after restoration [2,3]. The corrosion characteristics of metal alloys are dependent on the composition of the alloy, its potential values, the strain, the surface roughness, the degree of oxidation, the pH, the temperature of the media, the mixing velocity of the solution and the presence of inhibitors [4]. And it is all known that the oral cavity is a dynamic environment, subjecting to changes in pH and temperature, a continuous flow of saliva, microbiological activity, occlusal load, diet, unconscious regular contact with metal ions (contact with jewelry and cooking utensils), as well as many other factors [5]. Once the metal prosthesis is worn in mouth, the metal ions would release to oral cavity and then come to contact with cells and tissues in the immediate environment, or be distributed throughout the body [6,7]. And the metal ions released from dental alloys not only produced adverse effects on the morphology, viability and proliferation rate of gingival fibroblasts but also caused increased levels of Interleukin 2(IL-2) and Interleukin 6(IL-6) [8–12].

Foundation item: Projects (13ZR1427700, 13ZR1427900) supported by the Natural Science Foundation of Shanghai, China; Project (51304136) supported by the National Natural Science Foundation of China; Projects (S1414049, S1414050) supported by the Shanghai Education Development Foundation “Selection and Training the Excellent Young College Teacher” Project, China

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DOI: 10.1016/S1003-6326(16)64238-3

Tooth bleaching is an increasingly popular aesthetic procedure used in dentistry [13–17]. It is relatively simple and highly effective, and can often preclude the need for operative intervention [13,14]. There are various agents available for bleaching vital teeth, although they invariably involve the application or generation of hydrogen peroxide (HP), a strong oxidising agent. Despite increased popularity, controversy surrounds the use of peroxide-based bleaching systems to whiten teeth. The situation has not been helped by conflicting reports in the scientific literature and media, further compounded by a lack of standardisation in methodology or presentation of data. Some studies suggested the relatively high concentrations of peroxide used for topical bleaching altered the chemical structure of tooth tissues [15–18]. While vital bleaching does not appear to cause macroscopic changes to the dental hard tissues, microscopic changes have been reported, particularly where peroxide was applied at high concentrations [19,20].

Several bleaching methods exist, including in office bleaching with or without a light source [21,22], e.g., mouth guard bleaching under supervision of a dentist, and bleaching kits that were sold over the counter (where individuals apply the bleaching agent without the supervision of the dentist). Active HP concentrations may, however, vary enormously and can be as high as 35% [23] even though current UK law limits the peroxide content to 0.1%. Despite widespread debate, there is currently a trend towards employing greater concentrations of H₂O₂ as the active agent in tooth bleaching preparations [24,25]. Microstructural evaluation and corrosion properties of dental alloys subjected to bleaching have been investigated, and surface topographic alterations of Ni–Cr alloys occurred as a result of the application of 10% and 35% carbamide peroxide (CP) simulating at-home bleaching and in office bleaching during 14 d, respectively [26]. Ni–Cr alloys showed the highest surface roughness for both the control and home bleached subgroups [27,28].

The aim of the present study was therefore to investigate the effect of increasing H₂O₂ concentrations (0–30%) on surface properties from Ni–Cr alloys. This research will provide data in informing current discussion and scientific debate regarding the safety and efficacy of tooth bleaching agents.

2 Experimental

2.1 Sample preparation

The Ni–Cr dental casting alloy (77.36% Ni, 12.27% Cr, 4.84% Mo, 5.53% other elements) was used in the present study. The alloy samples were manufactured to a circle sheet of 10 mm in diameter and 1.5 mm in

thickness, divided into 4 groups randomly, and then immersed in 0, 3.6%, 10%, and 30% H₂O₂ solution of pH 3 at (37±0.1) °C for 112 h. The immersion time of 112 h better reflects the actual clinical tooth bleach. The surface morphologies were observed by scanning electron microscopy (SEM), the surface roughness was detected by surface profile-meter (SPM), and the composition and structure of the passive film formed on the surface of nickel–chromium alloy were tested by X-ray photo-electron spectrometer (XPS). All measured data were statistically analyzed using one-way analysis of variance (ANOVA) and multiple comparisons test (LSD *post hoc* test) to examine the effect of the factor of hydrogen peroxide concentration.

2.2 Surface roughness

Following immersion test, the surface roughness of the samples was measured again using a surface profile-meter (SPM) that was calibrated by setting the appropriate zero setting prior to roughness measurement of the samples. The roughness of the uppermost surface was then measured by moving the stylus across its diameter. This procedure was repeated eight times for each sample, altering the orientation each time, and the results were averaged.

2.3 Surface analysis

X-ray photoelectron spectroscopy measurement was performed to analyze the composition and structure of the passive film formed on the surface of nickel–chromium alloy by means of a PHI 5000 photoelectron spectrometer (VersaProbe, Japan) with monochromatized Al K_α radiation (1486.6 eV). The take-off angle for photoelectron detection was set at 45° for the sample surface. The vacuum level of the analyzing chamber during measurement was of the order of 10⁻⁸ Pa. The XPS data were converted into VAMAS file format and imported into XPSPEAK software package for manipulation and curve-fitting.

2.4 Statistical analysis

A two-way ANOVA (element by concentration) revealed a significant interaction between concentration and elements ($p < 0.001$) indicating that difference between solutions was different across elements. The two-way ANOVA was followed by a one-way ANOVA and Dunnett Post Hoc test for multiple comparisons between solutions for each element. The roughness measurements were analyzed using a paired t-test.

3 Results and discussion

3.1 Surface morphology

Figure 1 shows the surface morphology of the dental Ni–Cr casting alloy after being immersed in

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