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ORIGINAL ARTICLE

The effect of simulating porcelain firing on the elemental composition, microstructure, and mechanical properties of electroformed gold restorations

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Abstract *Background/purpose:* The mechanical properties of pure gold (Au) are modified by thermal treatments. Thus, the aim of this study was to evaluate the effect of porcelain firing on the elemental composition, microstructure, and mechanical properties of electroformed Au crowns.
Materials and methods: Twenty electroformed Au specimens were prepared and divided into two groups. The first group did not receive any treatment (ELEC), and the other group was subjected to porcelain firing (PFIR). After metallographic grinding and polishing, all were investigated by scanning electron microscopy, and elemental composition was determined using energy-dispersive X-ray spectroscopy (EDX). Internal porosity was identified by quantitative image processing. Mechanical properties including Martens hardness (HM), indentation modulus (E_{IT}), elastic index (η_{IT}), and Vickers hardness (HV) were determined by instrumented indentation testing. The results were statistically analyzed using unpaired *t* test ($\alpha = 0.05$).
Results: A random distribution of tiny pores was identified in cross section, but no significant difference was found between groups [ELEC (%), 0.24 ± 0.13; PFIR (%), 0.31 ± 0.7]. Backscattered electron images revealed no mean atomic number contrast for both groups, indicating that the material was a single-phase alloy, whereas no differences between groups were

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identified in the composition of C, N, O, and Au after EDX analysis. By contrast, all mechanical properties tested showed statistically significant differences, with the PFIR group showing significantly lower HM, η_{IT}, and HV but increased E_{IT} compared with those of the ELEC group. *Conclusion:* Although microstructure and elemental composition of electroformed Au crowns remain unchanged, the mechanical properties are significantly affected by the thermal treatment of porcelain firing.

Introduction

Electroforming has been adopted by dental technology since 1991 for the manufacture of gold (Au)-based metallic substrates for metalloceramic and telescopic crowns.[1–4] Metallic substrates made of electroformed Au are free of pores,[3] with excellent corrosion resistance and biocompatibility,[5] and with adequate to excellent marginal accuracy.[6–9] Low bond strength with dental porcelains,[10,11] technique sensitivity,[3] and the low mechanical properties of pure Au are among the drawbacks of this technology. However, analysis of clinical data has shown adequate longevity of electroformed crowns in both anterior and posterior regions.[12–14]

Although these structures are characterized as free of pores,[3] their mechanical properties are of great concern, because they are composed of a thin foil of pure Au with 0.2-mm mean thickness.[6] The mechanical properties of a substrate are of paramount importance for the performance of both telescopic crowns and galvanoceramic restorations, but until now there have been no studies on the mechanical properties of electroformed structures themselves. One serious limitation to conducting such studies is associated with sample preparation. Conventional mechanical tests (i.e., tensile, bending, and other tests) require bulky specimens, which cannot be prepared by electroforming technology, because the maximum achievable thickness is $<$0.3 mm.[3,10] As an alternative to conventional testing, the instrumented indentation test (IIT) has been determined by the International Organization for Standardization (ISO) as a reliable methodology for testing mechanical properties such as hardness, elastic index, relaxation, modulus of elasticity, and creep.[15] The principle of the technique is based on monitoring, in real time, the force applied to a hardness indenter and the indentation depth of the indenter in the sample. One advantage of this methodology is that irregular and small samples can be tested, thereby eliminating the need for bulky specimens.

In addition, previous studies have reported that electroformed structures contain light elements such as C, O, and N, which are retained in their structure, probably during the manufacturing process.[10] These low-atomic-number elements with small atomic radii can be dissolved in a metallic structure, forming an interstitial solid solution with increased hardness and tensile strength at the expense of ductility and fracture strength, as in the case of hydrogen embrittlement.[16] In addition, they might be implicated in further changes in mechanical properties during porcelain firing, because the firing temperature (780°C) is very close to the melting point of pure Au (1064°C), and various mechanisms might be triggered. N and O might evaporate during firing because of the degassing effect of vacuum, a technology extensively used to remove contaminating substances from metals and alloys (i.e., the removal of H_2 from Ti).[17] Thermal treatment might trigger the precipitation of new phases, modifying the microstructure and thus the mechanical properties. Interestingly, previous studies have shown that the mechanical properties of pure Au do indeed change after annealing above 300°C.[18] If this is a true hypothesis, then mechanical properties might be further modified with thermal treatment to enhance the performance of electroformed Au structures in telescopic and metalloceramic applications.

Therefore, the aim of this study was to determine the effect of porcelain firing on the elemental composition, microstructure, and mechanical properties of electroformed galvanic crowns. The null hypothesis was that the mechanical properties of electroformed Au structures are changed after porcelain firing.

Materials and methods

Sample preparation

One master silicone mold was prepared by the taking of an impression of a stainless steel rod (4 mm diameter and 5 mm high) with polyether materials (Impregum; 3M ESPE, St. Paul, MN, USA). Twenty cylindrical master dies were prepared by the pouring of a die stone (Jade Stone; Whip Mix Corporation, Louisville, KY, USA) into the master mold, which was left to set at ambient conditions. Then, 20 electroformed Au specimens were prepared (Figure 1) on the master dies in an electroforming machine (Ephos Galvano; Elemental Dental, Thessaloniki, Greece). The 20 specimens were equally divided into two groups. The first group received no further treatment (ELEC), and the second group (PFIR) was subjected to a complete firing schedule according to that used for a low-fusing porcelain (DuceraGold; Degudent, Hanau-Wolfgang, Germany) suitable for covering electroformed Au crowns. The firing schedule simulates two layers of opaque and dentin and a single glaze according to the manufacturer's instructions (Table 1). The firing of crowns were carried out in a dental oven (MultimatNTpress; Dentsply, York, PA, USA)

All specimens were then embedded along their longitudinal axis in an epoxy resin (Epofix; Struers, Belarup,

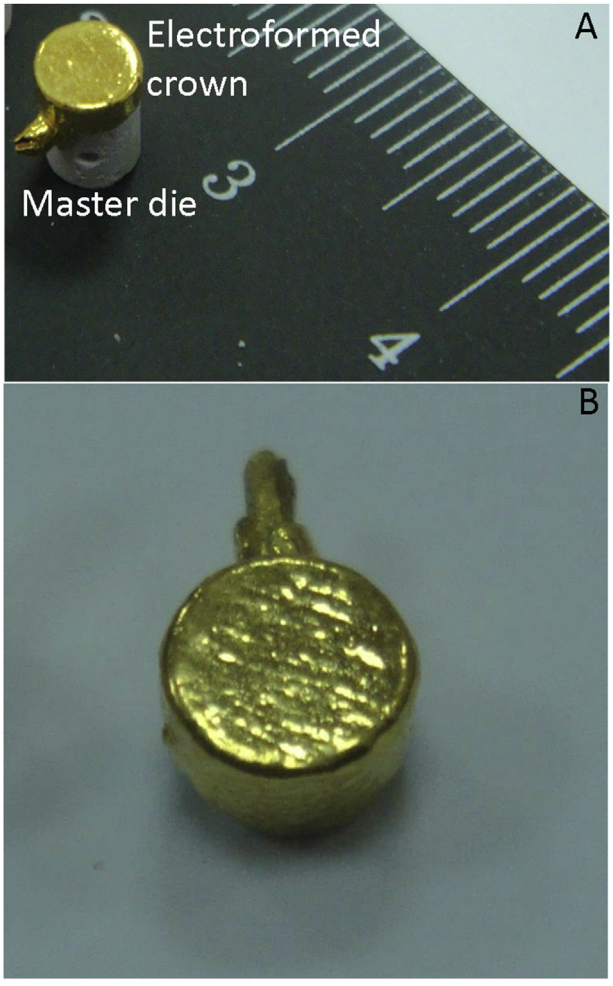

Figure 1 (A) Macroscopic images from specimen and master die used for the specimen preparation. Scale = 1 cm. (B) A close-up view of the specimen.

Denmark). After 24 hours of storage at room temperature, the specimens were ground with silicon carbide papers (from #220 to #2000 grit) under continuous water cooling in a grinding/polishing machine (Dap-V, Struers), polished with 3-μm, 0.5-μm, and 0.25-μm diamond paste (DP Paste, Struers), and ultrasonically cleaned for 5 minutes in a water bath.

Scanning electron microscopy/energy-dispersive X-ray spectroscopy

All specimens were investigated using scanning electron microscopy (Quanta 200; FEI, Hillsboro, OR, USA) with a secondary electron and backscattered electron (BE) detector at 25 kV accelerating voltage, 102 μA beam current, 10^{-6} Torr chamber pressure, and 6000× nominal magnification. The pores were discriminated based on image contrast, and the percentage porosity (area of pores on the cross section divided by the total cross-sectional area) was determined using image analysis software (XT Docu ver3.2; Soft Imaging System GmbH, FEI, Hillsboro, OR, USA). Three images were taken from each specimen, and the mean value of porosity was used to characterize each specimen of the group. One energy-dispersive X-ray spectroscopy (EDX) spectrum was collected from each specimen via an X Flash 6|10 Silicon Drift Detector (SDD; Bruker, Berlin, Germany) with a slew window, 8 kV accelerating voltage, 106 μA beam current, 500-second acquisition time, and 200 μm × 200 μm collecting window. Quantitative analysis was done using ZAF (atomic number, absorbance, fluorescence) correction factors with the dedicated software (ESPRIT ver. 1.9, Bruker).

Mechanical testing

The mechanical characterization of both groups was tested using the IIT with a universal hardness testing machine, ZHU0.2/Z2.5 (Zwick Roell, Ulm, Germany). The force—indentation depth curves were monitored by the application of 2.94N with a 2-second dwell time by a Vickers indenter. Three readings were taken for each specimen, and the mean value was taken as representative of the specimen itself and used for further statistical analysis. Based on force—indentation depth curves, the Martens hardness (HM), the indentation modulus (E_{IT}), and a percentage of the elastic portion of indentation (η_{IT}), also known as the elastic index, were determined using the appropriate mathematical formulas provided by the ISO 14577-1 specification.[15] After force removal, the Vickers hardness (HV) was determined by measurement of the diagonal length with a 20× magnification lens.

Statistical analysis

The results of porosity, C, N, O, and Au content and mechanical properties (HM, HV, E_{IT}, and η_{IT}) were statistically compared between the two groups using unpaired *t* test at a 95% level of significance ($\alpha = 0.05$).

Results

Figure 2A illustrates a representative secondary electron image from both groups tested with a few small pores. In Figure 2B, the pores have been discriminated from the bulk based on image contrast and marked in black. A

Table 1 Firing program for opaque, dentin, and glaze layers of DuceraGold porcelain.

Layer	Preheating temperature (°C)	Drying time (min)	Preheating time (min)	Heating rate (°/min)	Firing temperature (°C)	Firing time (min)	Vacuum
Opaque	575	2:00	3:00	55	780	2:00	Yes
Dentin	450	3:00	3:00	55	780	2:00	Yes
Glaze	450	2:00	3:00	55	770	1:00	No

representative BE image is illustrated in Figure 2C and shows no mean atomic number contrast. No statistically significant differences were identified, either for porosity (ELEC, 0.24 ± 0.13; PFIR, 0.31 ± 0.7, $P > 0.05$) or for elemental composition between the groups tested (Table 2). An EDX spectrum with the characteristic peaks of C, N, O, and Au can be seen in Figure 3.

Figure 4 illustrates the representative force—indentation depth curves for both groups tested. The peak of the PFIR group is shifted to the right, denoting a softer material, whereas the steeper (more vertical) unloading curve indicates a higher E_{IT}. All mechanical properties tested showed statistically significant differences between the groups, as presented in Table 3. The PFIR group showed significantly lower HM, η_{IT}, and HV but increased E_{IT}.

Table 2 Mean values and standard deviations in parentheses for both groups tested after EDX analysis ($n = 10$) without statistically significant differences ($P > 0.05$).

Group	C	N	O	Au
ELEC	2.9 (0.7)	0.2 (0.0)	0.2 (0.1)	96.7 (0.8)
PFIR	2.7 (0.6)	0.2 (0.1)	0.2 (0.1)	96.9 (0.8)

EDX = energy-dispersive X-ray spectroscopy; ELEC = first group, received no further treatment; PFIR = second group, subjected to a complete firing schedule.

Discussion

According to the results of this study, the null hypothesis must be accepted, as all mechanical properties were significantly changed after the porcelain firing simulation.

A limited amount of porosity was identified in cross section analysis in both groups, verifying previous reports[3] that electroformed crowns are free of gross internal pores. This is appended to the fact that the electroformed structures were built up layer by layer, eliminating the development of internal porosity. In accordance with reports from previous studies,[10] the traces of C, N, and O identified after EDX analysis were appended to the amine compound of the sulfite electrolyte.[5] Although the results of EDX analysis are presented in a quantitative manner, the values of light elements (such as C) cannot be considered accurate, because EDX has limited accuracy in the quantification of light elements in a nonstandard analysis.[19] Although not quantitatively accurate, the X-ray counts are directly comparable between the two groups tested, because the spectra were acquired under the same conditions (accelerating voltage, beam current, acquisition time, etc.) and were subjected to the same matrix effect,[19] and thus can be used for comparison purposes. C demonstrated higher content than did N and O (Table 2), a finding that might be appended to the minimal dissolution of C in Au (0.08 at%), whereas for the other two elements (N and O), their dissolution in Au is considered extremely low and has not yet been identified.[20] However, the presence of the aforementioned elements might also be appended to the retention of the amine molecule in the electroformed structure, and thus it will be worthwhile to analyze the chemical state of the aforementioned elements with further testing such as X-ray photoelectron spectroscopy analysis. Given that the elemental composition remained unchanged, the hypothesis that thermal treatment during porcelain firing might be used as a degassing procedure should be rejected. In addition, as no differences were identified in BE, no precipitation of new phases occurred during this procedure. However, these phases might be tiny, and thus the microstructure must be further tested using advanced techniques such as transmission electron microscopy analysis.

To the best of our knowledge, the dental literature contains no reports dealing with the mechanical properties of electroformed Au structures, and thus comparisons with previous results cannot be made. Two different hardness values, Martens and Vickers, were recorded. The HM is derived by a fully automated procedure during the loading—unloading cycle and is free from any complication associated with elastic recovery around indentations,[21] whereas HV is a widely used method and thus is useful for comparison purposes with literature data.[22] With both

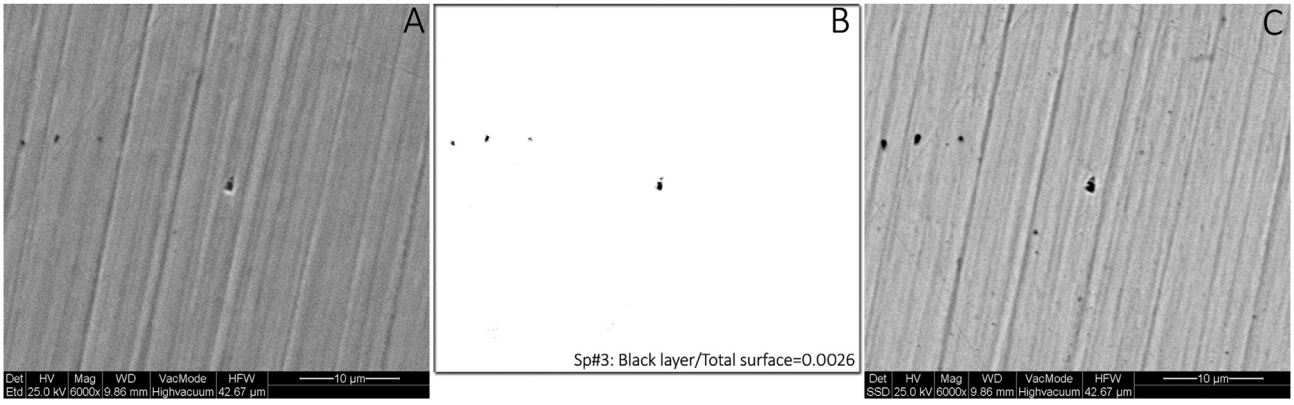

Figure 2 (A) Representative secondary electron image from both groups tested. A random distribution of small pores can be identified. (B) The pores have been discriminated based on image contrast and marked with black for further image processing. (C) Backscattered electron image revealed no mean atomic number contrast, denoting that the material is a single-phase alloy. (Original magnification, ×6000; bar, 10 µm.)

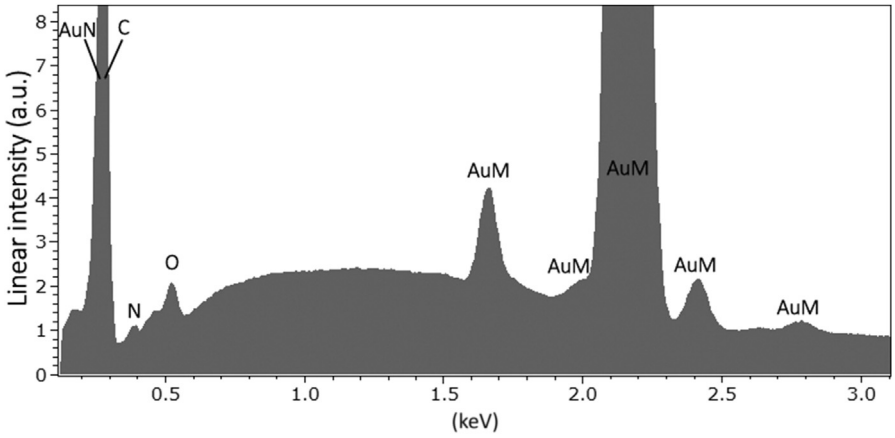

Figure 3 Representative X-ray energy-dispersive spectroscopy (EDX) spectrum from the cross section of both groups tested with the presence of C, N, and O apart from Au. AuM and AuN stand for the contribution of X-rays given off as electron return to the M and N shells respectively.

methods, hardness decreased after porcelain firing. Both groups showed HV values higher than that of pure Au (22 HV),[22] a finding that should be appended to the strengthening of light elements and/or the residual stress field developed during the manufacturing process.[23] Given that there were no elemental alterations after porcelain firing, the decrease in HV should be appended to the attenuation of residual stresses. E_{IT} was significantly changed after firing, a completely unexpected finding, because Young's modulus of pure Au is not affected by thermal treatment.[24] In addition, the determined values are less than half of those given for Young's modulus (79 GPa)[25] of pure Au. This inconsistency should be appended to the fact that the determination of E_{IT} is strongly affected by the presence of residual stresses, and thus the E_{IT} cannot be accurately determined in stress-free samples.[26] The decrease in elastic index for the PFIR group denotes a more ductile structure that is appended to the attenuation of residual stress fields after porcelain firing.[22]

Although there is no direct proof, the aforementioned analyses concur that the mechanical properties of electroformed Au structures affected by porcelain firing due to the relief of residual stress were developed during the manufacturing process. Therefore, the clinical implications of this study are that if electroformed structures are made for telescopic crowns, any further thermal treatment should be avoided, because higher hardness increases the friction coefficient and thus the adhesive friction between the male and female telescopic crowns. In addition, increased hardness better withstands wear over successive placements—removals in the oral cavity. In metalloceramic applications, porcelain firing should be kept to a minimum as much as possible to avoid further decreases in mechanical properties. Interestingly, there is no relevant study regarding the analysis of this residual stress field in electroformed structures, and this remains an interesting field for further research. Another approach is that the addition of special agents to the electroforming solution might provide further increases in mechanical properties through the retention of these elements in the electroformed structures. Although microstructure and elemental composition of electroformed Au crowns remain unchanged, the mechanical properties are significantly affected by thermal treatment of porcelain firing and thus, there is still room for further research and development on electroforming technology to increase its efficacy in fixed and removable restorations.

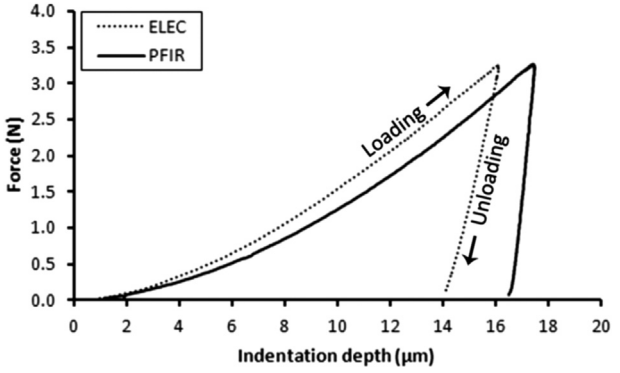

Figure 4 Representative force—indentation depth curves for both groups included in the study. ELEC = first group, received no further treatment; PFIR = second group, subjected to a complete firing schedule.

Table 3 Mean values and standard deviations in parentheses of Martens hardness (HM), indentation modulus (E_{IT}), elastic index (η_{IT}), and Vickers hardness (HV; $n = 10$) along with P values.

Group	HM (N/mm^2)	E_{IT} (GPa)	η_{IT} (%)	HV
ELEC	476 (22)	17.8 (1.6)	16.1 (1.5)	47 (4)
PFIR	369 (31)	30.6 (6.6)	7.7 (1.6)	34 (2)
P	<0.001	<0.001	<0.001	<0.001

All mechanical properties demonstrated statistically significant differences between the groups tested.
ELEC = first group, received no further treatment; PFIR = second group, subjected to a complete firing schedule.

Conflicts of interest

The authors have no conflicts of interest relevant to this article.

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