



# Properties of experimental copper-aluminium-nickel alloys for dental post-and-core applications

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**PURPOSE.** This study aimed to develop a copper-aluminium-nickel alloy which has properties comparable to that of dental alloys used for dental post and core applications with the reasonable cost. **MATERIALS AND METHODS.** Sixteen groups of experimental copper alloys with variants of 3, 6, 9, 12 wt% Al and 0, 2, 4, 6 wt% Ni were prepared and casted. Their properties were tested and evaluated. The data of thermal, physical, and mechanical properties were analyzed using the two-way ANOVA and Tukey's test ( $\alpha=0.05$ ). The alloy toxicity was evaluated according to the ISO standard. **RESULTS.** The solidus and liquidus points of experimental alloys ranged from 1023°C to 1113°C and increased as the nickel content increased. The highest ultimate tensile strength (595.9 ± 14.2 MPa) was shown in the Cu-12Al-4Ni alloy. The tensile strength was increased as the both elements increased. Alloys with 3-6 wt% Al exhibited a small amount of 0.2% proof strength. Accordingly, the Cu-9Al-2Ni and Cu-9Al-4Ni alloys not only demonstrated an appropriate modulus of elasticity (113.9 ± 8.0 and 122.8 ± 11.3 GPa, respectively), but also had a value of 0.2% proof strength (190.8 ± 4.8 and 198.2 ± 3.4 MPa, respectively), which complied with the ISO standard requirement (>180 MPa). Alloys with the highest contents of nickel (6 wt% Ni) revealed a widespread decolourisation zone (5.0-5.9 mm), which correspondingly produced the largest cell response, equating positive control. **CONCLUSION.** The copper alloys fused with 9 wt% Al and 2-4 wt% Ni can be considered for a potential use as dental post and core applications. [J Adv Prosthodont 2014;6:215-23]

**KEY WORDS:** Cu-Al-Ni alloy; Copper alloy; Dental alloy; Post and core

## INTRODUCTION

Dental post and core are usually fabricated from a cast alloy as a single unit from a lost-wax technique. The posts, originally designed to retain an artificial crown, have been shown as a system which provides fracture resistance to the roots.<sup>1</sup> They reproduce the contours of the prepared root

canal and adapt well to the canal morphology, especially when the root canal is irregularly shaped. An ideal post and core material should allow any failure to occur in the bulk material before damage occurs to the tooth structure when it is subjected to chewing forces.<sup>2</sup> It has been reported in some studies that when a system with components having different rigidity is loaded, then the more rigid component is capable of resisting greater forces without distortion.<sup>3,4</sup> Insufficient stiffness of a post permits micro-movement of the core and thus, during function, distortion of the restoration at the margins occurs. However, the post must not be too stiff, in that it cannot deform compatibly with the root structure under functional loads. It has been suggested that a post should have a modulus of elasticity close to that of human dentin, in order to distribute applied forces evenly along the length of the post.<sup>5-7</sup> Anusavice<sup>8</sup> has established that the elastic modulus of gold alloys (*circa* 90 GPa) is the closest to that of dentin. However, these alloys are too expensive to be employed as a post and core, and cannot be

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supported by many patients.

Dental posts and cores, in a clinical situation, are in a closed environment. They are encapsulated within luting cement, the root structure and the crown restorations. Some luting cement may form an insoluble film, which covers the posts and cores and completely prevents them from making contact with the dentinal fluid, which in turn leads to potential corrosion of the posts.<sup>9</sup> Furthermore, nickel has a much higher electromotive force than copper, and so it is anticipated that the addition of nickel to a copper-aluminium alloy will be able to greatly improve the corrosion resistance and electrochemical abilities of posts and cores, and therefore resist attacks from the biological environment. In addition, Cu-Al-Ni alloy is perceived to be a significant corrosion-resistant material. It is used in marine hardware, for handling seawater, and in the industrial processing fluids.<sup>10</sup> Because it is very reasonable in price, this Cu-Al-Ni alloy could be developed for potential use in the dental post-and-core application.

**MATERIALS AND METHODS**

Sixteen groups of experimental alloys with varying proportions of Cu, Al and Ni were prepared, and the details of all groups are summarized in Table 1.

Highly purified (>99.99%) copper droplets, and aluminium and nickel beads (Wako Pure Chemical Industries Ltd., Chuo, Osaka, Japan) were used in this study. Each group weighed 35 g, with the calculated amounts of all elements established by using an analytical balance (Precisa 262 SMA-FR, Precisa Instruments AG, Dietikon, Switzerland). The elements were melted together inside a 25 mm diameter cylindrical graphite crucible, contained within a fused silica crucible sleeve, using a vacuum induction casting unit (Linn HFS 3 Vacutherm, Linn High Therm GmbH, Eschenfelden, Germany). The vacuum was measured at approximately 50 mbar, and ultra-high purity argon was then fed in during the procedure. The ingot was bench-cooled within the crucible, and covered with a graphite cap.

The alloy compositions were determined after melting using a scanning electron microscope (JSM 4510 LV, JEOL Ltd., Akishima, Tokyo, Japan) and energy dispersion scanning (INCA x-act, Oxford Instruments PLC., Abingdon,

Oxfordshire, UK). The solidus, liquidus and melting range of each alloy was evaluated using a differential scanning calorimeter (DSC8270, Rigaku Corporation, Shibuya, Tokyo, Japan). Approximately 1 g of each sample was heated at a rate of 10°C/min, extended to 1300°C. The measurements were made using “d\*TREK” software (Rigagu Corporation, Shibuya, Tokyo, Japan) on six samples for each group.

A ‘PMMA sheet’ (Sumipex TL, SumiplexTechsheet Co., Ltd., Kaosiung, Taiwan) was cut into smaller specimen patterns, 10 mm × 10 mm × 2 mm, to be used for corrosion, hardness and static immersion testing. The tensile dumbbell preformed patterns, with a screw threaded end, diameter of 3 mm and 18 mm in gauge length, in accordance with ISO standard (ISO 22674:2006),<sup>11</sup> were constructed in a split-silicone mould (Xiameter RTV-3481, Dow Corning Corp., Midland, MI, US) using an acetal copolymer rod (Ertacetal C, Dotmar EPP Pty. Ltd., Acacia Ridge, QLD, Australia), and combined the screw thread via the injection of a molten blue inlay wax (Type II, Class I, Kerr Corporation, Romulus, MI, USA).

The whole patterns were constructed and invested in cristobalite investment (Cristobalite PF, Shofu Incorporated, Higashiyama, Kyoto, Japan) using a vacuum mixing device (Vacuret-S, ReitelFeinwerktechnik GmbH, Bad Essen, Germany). The casting of all specimens was performed in a vacuum induction casting unit (Linn HFS 3 Vacutherm, Linn High Therm GmbH, Eschenfelden, Germany). Five impeccable specimens were prepared from each alloy for each test.

Five specimens (10 mm × 10 mm × 2 mm) of each group were mounted in epoxy resin (EpoKwick, Buehler, An ITW Company, Lake Bluff, IL, USA). The surface of each specimen was flattened and finished using a metallographic grinder/polisher (Rotopol-21, Struers A/S, Copenhagen, Denmark) through a standard metallographic procedure, starting from FEPA P 200 to FEPA P 2000 silicon carbide paper (CarbiMet 2, Buehler, An ITW Company, Lake Bluff, IL, USA), and finished with 1 µm diamond paste (Meta DI, Buehler, An ITW Company, Lake Bluff, IL, USA).

The surface hardness was determined using a micro-hardness tester (FM-700, Future-tech Corporation, Kawasaki, Kanakawa, Japan) via a Vickers’ indenter con-

**Table 1.** Sixteen experimental alloy group identifiers and element compositions used in this study

		Ni (Weight %)			
		0	2	4	6
Al (Weight %)	3	Cu-3Al-0Ni	Cu-3Al-2Ni	Cu-3Al-4Ni	Cu-3Al-6Ni
	6	Cu-6Al-0Ni	Cu-6Al-2Ni	Cu-6Al-4Ni	Cu-6Al-6Ni
	9	Cu-9Al-0Ni	Cu-9Al-2Ni	Cu-9Al-4Ni	Cu-9Al-6Ni
	12	Cu-12Al-0Ni	Cu-12Al-2Ni	Cu-12Al-4Ni	Cu-12Al-6Ni
Cu balanced					

trollable load of 1 Kgf for 15 sec. Five readings were carried out in the center and the corner regions of each specimen. All records were collected and analyzed statistically.

Five dumbbell specimens were loaded in tension using a universal testing machine (Model 5566, Instron Corporation, High Wycombe, Buckinghamshire, UK) at a crosshead speed of  $1.5 \pm 0.5$  mm/min at room temperature ( $23 \pm 1^\circ\text{C}$ ) until a fracture occurred.

The ultimate tensile strength, proof strength at a 0.2% offset, modulus of elasticity and the percentage elongation were determined and recorded.

Two square specimens ( $10\text{ mm} \times 10\text{ mm} \times 2\text{ mm}$ ) from each group were attached with stainless steel nuts using conductive silver epoxy resin (Fast Setting #05062-AB, SPI Supplies/Structure Probe Incorporated, West Chester, PA, USA). Next, the whole assembly was covered with an electrically insulating epoxy binder (UHU 2, Adhesives, UHU GmbH & Co. KG, Bühl/Baden, Germany) also embedded in epoxy resin (EpoKwick, Buehler, An ITW Company, Lake Bluff, IL, USA). The exposed surfaces of the embedded specimens were prepared with a grinder/polisher (Rotopol-21, Struers A/S, Copenhagen, Denmark) using a standard metallographic procedure, ending with FEPA P 4000 wetted silicon carbide paper. The exposed area of the test specimens was approximately  $100\text{ mm}^2$ . The specimens were then ultrasonically cleaned in 95% ethanol for 1 minute.

The experiment was carried out in a 0.9% sodium chloride electrolyte ( $\text{pH } 7.4 \pm 1$ ), within double-walled corrosion cell at  $37^\circ\text{C}$ , using a saturated calomel electrode (SCE) and platinum wire as a reference and counter electrode. The temperature was controlled via circulated water passing through the cell wall, using a thermostatically controlled water bath (A10, Thermo Scientific Incorporated, Waltham, MA, USA). The electrodes were connected to a Potentiostat/Galvanostat (Solartron 1285A, Farnborough, Hampshire, UK). The measurement was monitored using electrochemical software (CorrWare and CorrView Version 3.20b, Scribner Associates Inc., Southern Pines, NC, USA).

Bubbled nitrogen gas was then produced through the electrolyte, at a rate of  $100\text{ cm}^3/\text{min}$  for at least 30 minutes, and then streamed into the cell. The open circuit potential ( $E_{\text{ocp}}$ ) was registered for 2 hours. Subsequently, the potentiodynamic was scanned for 5 minutes after finishing the  $E_{\text{ocp}}$  measurement, at a rate of  $1\text{ mV}/\text{sec}$  from  $-150\text{ mV}$  of  $E_{\text{ocp}}$  up to a potential of  $+1000\text{ mV}$ . The curvature of the  $E_{\text{ocp}}$  in mV (SCE), versus time, and the curve of potential versus the logarithm of current density, were both recorded.

Two quadrilateral specimens from each group, with a total surface area of approximately  $200\text{ mm}^2$ , were blasted using standard metallographic procedures, in order to remove the surfaces at least  $0.1\text{ mm}$  of material. Finally, FEPA P 4000 wet silicon carbide paper was employed. The surface area of each specimen was recorded, ultrasonically cleaned in 95% ethanol for 1 minute, rinsed in distilled water, and then dried with oil-free compressed air. An aqueous solution comprising  $0.1\text{ mol/L}$  lactic acid and  $0.1\text{ mol/L}$  sodium chloride, with a pH value in the range of 2.2

to 2.4, was prepared immediately before use.

A 100 mL bottle (SCHOTT Duran, Duran Productions GmbH & Co. KG, Hattenbergstraße, Mainz, Germany) was used to contain the aqueous solution. Each test specimen was suspended by being hung on nylon strings in separate bottles, at  $37 \pm 1^\circ\text{C}$ , for 7 days. The bottles were tightly sealed to prevent evaporation. After 7 days all specimens were removed, and the test solutions were collected and analyzed separately using Atomic Absorption Spectrometry (Varian SpectrAA-200, Varian Semiconductor Equipment, Gloucester, CA, USA). The values of each observed element were recorded in  $\mu\text{g}/\text{cm}^2/7\text{d}$ .

Six specimens from each group were cut from the sprues of the dumbbell casting. All sides of the specimens were removed using FEPA P 1000 silicon carbide paper, in order to create sample discs measuring  $5\text{ mm}$  diameter and  $1\text{ mm}$  thickness. The specimens were ultrasonically cleaned in 95% ethanol for 1 minute, rinsed with distilled water and then dried with oil-free compressed air.

The cytotoxicity was tested following the general guidelines presented in ISO 10993-5:1999.<sup>12</sup> The L929 (NCTC Clone, ATCC Lot. 2869501, Passage No. 556, American Type Culture Collection, Manassas, VA, USA) was used for the cell line. The monolayer of cell line was suspended in 3% agar (Calbiochem 12177 Agar, Merck KGaA, Darmstadt, Germany) in order to obtain a final concentration of approximately  $3 \times 10^5$  cells/mL, and was prepared in a  $90\text{ mm}$  diameter culture dish (Corning Dish, Corning Incorporated, Corning, NY, USA). Ten milliliters of L929 cells, with an intensity of  $2.5 \times 10^5$  cells per  $\text{cm}^3$  in a completing cultured DMEM medium (Gibco DMEM, Invitrogen Corporation, Carlsbad, CA, USA), were then applied into the dish. The dish was incubated in a  $\text{CO}_2$  incubator (Thermo Scientific Forma Series II, Thermo Fisher Scientific Incorporated, Marietta, OH, USA) with 5.0%  $\text{CO}_2$  and 95% relative humidity, at  $37^\circ\text{C}$ , for 24 hours. The cell style developed as a monolayer, and then removed the cultured medium. The culture dish was then refilled with new more of the agar cultured medium with contains completed  $2 \times \text{DMEM}$  medium and 3% agar. The cultured dish was left until the agar cultured medium became stiff, and it was then dyed with 1% neutral red indicator ( $\text{C}_{15}\text{H}_{17}\text{ClN}_4$ , C.I. 50040, Merck KGaA, Darmstadt, Germany). The area within the cultured dish was then divided into 4 sectors (testing zones), and controlled specimens of positive disc (Polyurethane film-ZDEC: RM-A, Hatano Research Institute, Kanakawa, Japan) and negative disc (Thermanox, Thermo Fisher Scientific Incorporated, New York, NY, USA) were located on the upper right and upper left testing zones, accordingly. The bottom two testing zones provided the sample discs. The culture dish was again incubated, in an incubator with 5.0%  $\text{CO}_2$  and 95% relative humidity, at  $37^\circ\text{C}$ , for 24 hours. The decolorized zones and cell lysis were recorded under an inverted phase contrast microscope (Eclipse TS100, Nikon Corporation, Chiyoda, Tokyo, Japan). Consequently, the ratio of the decolorized zones and the cell lysis were both calculated as a cell

response.

The data of the hardness, tensile strength, 0.2% proof stress, modulus of elasticity, percentage elongation and thermal property of the experimental alloys were analyzed using the two-way analysis of variance and Tukey's test, at a significance level of 0.05 (PASW Statistics 18.0.0, SPSS Inc., Chicago, IL, USA).

## RESULTS

The solidus and liquidus points increased as the nickel content increased. The influence of aluminium content was significantly higher when the aluminium content was at its lowest (3 wt% Al) as depicted in Fig. 1. The Cu-3Al-6Ni alloy showed the highest solidus and liquidus points (1069.2 ± 0.3°C and 1113.4 ± 1.5°C, respectively). Additionally, the lowest solidus and liquidus points, with the same nickel content, were exhibited by the 9 wt% Al alloy.

The widest melting ranges (46.3 ± 1.4, 35.1 ± 0.5, 32.7 ± 2.0 and 44.2 ± 1.7°C), with the same nickel content, were measured in the alloys with the lowest aluminium content (3 wt% Al). Likewise, the narrowest melting ranges (27.7 ± 0.1, 28.9 ± 0.2, 26.9 ± 1.1 and 29.1 ± 0.1°C) were found in the alloys with the highest aluminium content (12 wt% Al). Accordingly, the melting ranges of the alloys decreased when the aluminium contents were increased. Furthermore, the melting ranges of the alloys with the same nickel content significantly decreased, once the content of aluminium reached more than 6% (Table 2).

According to the worst castability of the Cu-12Al-6Ni alloy, those castings could not be completely produced in this group. The physical and mechanical properties of this alloy were therefore discarded.

The surface hardness was influenced by both factors and their interaction which, correspondingly, increased as both elements increased. Aluminium demonstrated a higher degree of increase rather than nickel. The highest surface hardness (305.9 ± 2.5 HVN) was revealed in the Cu-12Al-4Ni alloy (Table 3).

The tensile strength was influenced by both factors without any effect upon interaction. It increased as the both elements increased. Again, Aluminium showed a higher degree of increase rather than nickel. The highest ultimate tensile strength (595.9 ± 14.2 MPa) was shown in the Cu-12Al-4Ni alloy.

Similarly, 0.2% proof stress was influenced by both factors and their interaction. The alloy with the highest aluminium content (12 wt% Al) showed a significant increase in the 0.2% proof stress, but the elongation was extremely limited.

Table 4 shows the results of cytotoxicity of the cells in the experimental alloys. All alloys exhibited moderately cytotoxicity, similar to the conventional alloys used in dentistry.<sup>13,14</sup> However, the higher content of nickel showed more decolorization zones. The highest content of nickel (6 wt% Ni) showed the widest decolorization zone (5.0-5.9 mm) that caused the decolorization index up to level three. This confirmed the negative effects of nickel in its biocompatibility.

As shown in Table 5, the elution of copper (0.18, 0.45, 0.91 and 0.37 µg/cm<sup>2</sup>/7d) seems to be faded out, when the aluminium content is increased to 9%. This result confirmed that aluminium was acting as a tarnished protector of the copper alloys. The amount of nickel leaching out increased when the nickel contents were increased. The lowest value (1.14, 5.45 and 6.13 µg/cm<sup>2</sup>/7d) was demon-

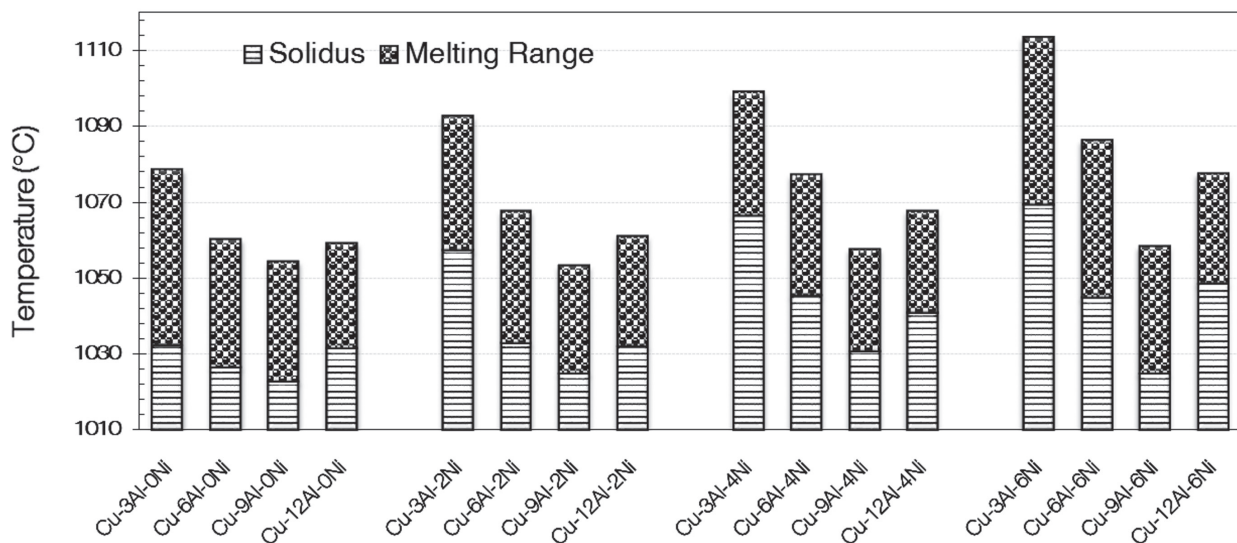


Fig. 1. Solidus, liquidus and melting ranges of experimental alloys.



**Table 2.** Thermal properties of experimental alloys

Material	Solidus (°C)	Liquidus (°C)	Melting range (°C)
C-3Al-0Ni	1032.3 (1.2) <sup>f</sup>	1078.6 (0.1) <sup>e</sup>	46.3 (1.4) <sup>g</sup>
C-6Al-0Ni	1026.5 (0.4) <sup>b</sup>	1060.1 (1.2) <sup>b</sup>	33.6 (1.4) <sup>c,d</sup>
C-9Al-0Ni	1022.7 (0.9) <sup>a</sup>	1054.5 (0.1) <sup>a</sup>	30.7 (0.4) <sup>a</sup>
C-12Al-0Ni	1031.5 (0.5) <sup>d,e</sup>	1059.1 (0.4) <sup>b,c</sup>	27.6 (0.1) <sup>a</sup>
C-3Al-2Ni	1057.4 (0.6) <sup>j</sup>	1092.5 (1.0) <sup>g</sup>	35.1 (0.5) <sup>d</sup>
C-6Al-2Ni	1032.8 (1.1) <sup>f</sup>	1067.8 (1.1) <sup>d</sup>	35.0 (0.1) <sup>d</sup>
C-9Al-2Ni	1024.8 (0.1) <sup>b</sup>	1053.3 (2.6) <sup>a</sup>	28.5 (2.9) <sup>a</sup>
C-12Al-2Ni	1032.1 (0.1) <sup>e,f</sup>	1061.0 (0.4) <sup>c</sup>	28.9 (0.2) <sup>a</sup>
C-3Al-4Ni	1066.4 (0.4) <sup>k</sup>	1099.0 (1.7) <sup>h</sup>	32.7 (2.0) <sup>b,c</sup>
C-6Al-4Ni	1045.2 (0.6) <sup>h</sup>	1077.2 (0.5) <sup>e</sup>	32.0 (0.8) <sup>b</sup>
C-9Al-4Ni	1030.8 (0.1) <sup>e</sup>	1057.7 (0.1) <sup>b</sup>	26.9 (0.1) <sup>a</sup>
C-12Al-4Ni	1040.9 (0.3) <sup>g</sup>	1067.8 (1.2) <sup>d</sup>	26.8 (1.1) <sup>a</sup>
C-3Al-6Ni	1069.2 (0.3) <sup>l</sup>	1113.4 (1.5) <sup>i</sup>	44.1 (1.7) <sup>f,g</sup>
C-6Al-6Ni	1044.7 (0.1) <sup>h</sup>	1086.2 (1.5) <sup>f</sup>	41.5 (1.7) <sup>e</sup>
C-9Al-6Ni	1029.5 (0.3) <sup>b</sup>	1058.3 (0.2) <sup>b</sup>	28.5 (0.9) <sup>a</sup>
C-12Al-6Ni	1048.6 (0.2) <sup>j</sup>	1077.6 (0.1) <sup>e</sup>	29.1 (0.1) <sup>a</sup>

Values are means (SD). Identical letters indicate no statistical difference ( $P < .05$ ).

**Table 3.** Summarizes the mechanical properties of the experimental alloy

Material	Tensile strength (MPa)	0.2% Proof stress (MPa)	Elastic modulus(GPa)	Elongation (%)	Hardness (HVN)
C-3Al-0Ni	197.3 (11.2) <sup>a</sup>	50.7 (3.3) <sup>a</sup>	67.3 (5.1) <sup>a,b</sup>	32.7 (2.5) <sup>c</sup>	50.6 (1.6) <sup>a</sup>
C-6Al-0Ni	189.4 (13.3) <sup>a</sup>	54.5 (3.7) <sup>a,b</sup>	66.6 (5.3) <sup>a,b</sup>	38.4(5.7) <sup>c,d,e</sup>	56.8 (1.2) <sup>b</sup>
C-9Al-0Ni	436.2 (25.5) <sup>c</sup>	168.0 (4.3) <sup>e</sup>	122.5 (12.1) <sup>d,e</sup>	19.4 (1.8) <sup>b</sup>	117.3 (0.9) <sup>e</sup>
C-12Al-0Ni	470.8 (60.2) <sup>c,d</sup>	-	94.5 (10.4) <sup>b,c,d</sup>	0.1 (0.1) <sup>a</sup>	279.1 (3.0) <sup>f</sup>
C-3Al-2Ni	209.8 (14.9) <sup>a</sup>	59.1 (5.4) <sup>a,b</sup>	98.3 (9.5) <sup>c,d</sup>	42.0 (3.9) <sup>d,e,f</sup>	54.0 (1.7) <sup>a,b</sup>
C-6Al-2Ni	210.0 (14.7) <sup>a</sup>	72.2 (2.6) <sup>b,c</sup>	97.4 (9.3) <sup>c,d</sup>	46.4 (6.6) <sup>e,f</sup>	63.9 (1.3) <sup>c</sup>
C-9Al-2Ni	504.6 (16.9) <sup>d,e</sup>	190.8 (4.8) <sup>f</sup>	113.9 (8.0) <sup>c,d</sup>	21.9 (2.1) <sup>b</sup>	128.5 (1.6) <sup>f</sup>
C-12Al-2Ni	480.2 (54.3) <sup>c,d,e</sup>	-	81.3 (5.3) <sup>a,b,c</sup>	0.1 (0.1) <sup>a</sup>	283.7 (3.0) <sup>f</sup>
C-3Al-4Ni	246.8 (21.2) <sup>a</sup>	57.8 (4.9) <sup>a,b</sup>	108.2 (10.7) <sup>c,d</sup>	45.1 (4.2) <sup>e,f</sup>	56.1 (1.0) <sup>b</sup>
C-6Al-4Ni	255.2 (25.8) <sup>a</sup>	86.3 (9.2) <sup>c</sup>	110.0 (7.9) <sup>c,d</sup>	47.4 (6.8) <sup>f</sup>	66.8 (2.7) <sup>c</sup>
C-9Al-4Ni	505.6 (13.0) <sup>d,e</sup>	198.2 (3.4) <sup>f</sup>	122.8 (11.3) <sup>d,e</sup>	23.3 (2.2) <sup>b</sup>	133.7 (1.1) <sup>g</sup>
C-12Al-4Ni	595.9 (14.2) <sup>f</sup>	507.6 (23.7) <sup>h</sup>	63.9 (4.0) <sup>a</sup>	1.7 (0.6) <sup>a</sup>	305.9 (2.5) <sup>k</sup>
C-3Al-6Ni	348.0 (44.7) <sup>b</sup>	141.6 (10.7) <sup>d</sup>	119.7 (25.5) <sup>d,e</sup>	35.5 (2.9) <sup>c,d</sup>	94.1 (1.1) <sup>d</sup>
C-6Al-6Ni	340.9 (37.8) <sup>b</sup>	147.0 (10.2) <sup>d</sup>	139.1 (14.2) <sup>e</sup>	33.1 (5.9) <sup>c</sup>	94.6 (2.0) <sup>d</sup>
C-9Al-6Ni	539.1 (27.2) <sup>e,f</sup>	246.4 (12.0) <sup>g</sup>	113.7 (12.0) <sup>d,e</sup>	20.4 (2.9) <sup>b</sup>	144.5 (1.1) <sup>h</sup>
C-12Al-6Ni			Rejected		

Values are means (SD). Identical letters indicate no statistical difference ( $P < .05$ ).

**Table 4.** Cytotoxicity of the experimental alloy evaluated by the Agar Overlay Test

Material	Decolorization zone (mm)	Decolorization index	Lysis index	Cell response	Cytotoxic interpretation
Negative	0.0	0	0	0/0	non
Positive	5.5	3	2	3/2	moderately
C-3Al-0Ni	3.4	2	2	2/2	moderately
C-6Al-0Ni	3.4	2	2	2/2	moderately
C-9Al-0Ni	3.9	2	2	2/2	moderately
C-12Al-0Ni	3.8	2	2	2/2	moderately
C-3Al-2Ni	4.0	2	2	2/2	moderately
C-6Al-2Ni	4.0	2	2	2/2	moderately
C-9Al-2Ni	3.9	2	2	2/2	moderately
C-12Al-2Ni	4.3	2	2	2/2	moderately
C-3Al-4Ni	4.5	2	2	2/2	moderately
C-6Al-4Ni	4.0	2	2	2/2	moderately
C-9Al-4Ni	4.5	2	2	2/2	moderately
C-12Al-4Ni	4.5	2	2	2/2	moderately
C-3Al-6Ni	5.9	3	2	3/2	moderately
C-6Al-6Ni	5.0	3	2	3/2	moderately
C-9Al-6Ni	5.3	3	2	3/2	moderately
C-12Al-6Ni			Rejected		

**Table 5.** Elution of elements presented in the test solution after seven days

Material	Cu	Al	Ni	Over all
		(mg/cm <sup>2</sup> /7d)		
C-3Al-0Ni	110.10	6.38	0.18	116.66
C-6Al-0Ni	127.70	15.97	0.22	143.89
C-9Al-0Ni	0.18	61.87	0.23	62.28
C-12Al-0Ni	0.11	81.70	0.22	82.03
C-3Al-2Ni	97.25	2.77	8.97	108.99
C-6Al-2Ni	31.15	11.21	1.44	43.80
C-9Al-2Ni	0.45	14.72	5.14	20.31
C-12Al-2Ni	0.05	42.66	7.37	50.07
C-3Al-4Ni	109.50	6.74	7.89	124.13
C-6Al-4Ni	93.24	6.82	5.45	105.51
C-9Al-4Ni	0.91	24.61	8.83	34.34
C-12Al-4Ni	0.34	38.35	11.54	50.23
C-3Al-6Ni	90.72	5.36	9.83	105.91
C-6Al-6Ni	35.02	3.37	6.13	44.52
C-9Al-6Ni	0.37	22.79	13.26	36.42
C-12Al-6Ni		Rejected		

strated in the 6 wt% Al alloys. Nevertheless, within the same nickel content alloys, the overall number of elements leaching out in 9 wt% Al groups (62.28, 20.31, 34.34 and 36.42 μg/cm<sup>2</sup>/7d) were lower than the others, and the Cu-9Al-2Ni alloy also demonstrated the lowest value (20.31 μg/cm<sup>2</sup>/7d).

The kinetics, thermodynamics and passivity of the experimental alloys are shown in Table 6. The open circuit potentials ( $E_{ocp}$ ) of the 9 wt% Al alloys (-214.4, -218.5 and -222.1 mV, SCE) existing have higher a potential than the others within the same groups, once the nickel content drops to less than 6%. Similarly, the corrosion potential ( $E_{corr}$ ) of these alloys (-281.6, -248.2 and -247.8 mV, SCE) exhibits the same manner as the open circuit potential ( $E_{ocp}$ ).

The potential of the passive region ( $E_p$ ) specifies the stability of the passive film, the higher value the better. The 6 wt% Al alloys presented the least value (94.1, 89.6, 84.7 and 116.5 mV, SCE) within the same nickel groups, and this meant that the passive film of these alloys was the easiest to breakdown and lose the oxide film, corresponding to their corrosion rates (0.01, 0.023, 0.035 and 0.031 mpy). The Cu-6Al-4Ni alloy revealed the highest corrosion rate.

There was not enough difference in cathodic current density ( $I_c$ ) and passive current density ( $I_p$ ) to determine the alloy passivity. On the one hand, the smaller cathodic current density ( $I_c$ ) in the passive region indicated a higher

**Table 6.** Results of the Electrochemical Corrosion Tests

Material	Kinetics	Thermodynamics		Passivity (Corrosion resistance)		
	Corrrate (mpy)	E <sub>ocp</sub> (mV, SCE)	E <sub>corr</sub> (mV, SCE)	I <sub>p</sub> (Amps/cm <sup>2</sup> )	I <sub>c</sub> (Amps/cm <sup>2</sup> )	E <sub>p</sub> (mV, SCE)
C-3Al-0Ni	0.0094	-292.1	-333.5	0.0021	0.0132	116.5
C-6Al-0Ni	0.0100	-247.7	-320.0	0.0066	0.0048	94.1
C-9Al-0Ni	0.0083	-214.4	-281.6	0.0028	0.0036	114.4
C-12Al-0Ni	0.0039	-256.9	-295.4	0.0022	0.0133	168.1
C-3Al-2Ni	0.0148	-247.4	-269.8	0.0020	0.0178	108.4
C-6Al-2Ni	0.0230	-236.3	-266.9	0.0030	0.0150	89.6
C-9Al-2Ni	0.0028	-218.5	-248.2	0.0014	0.0081	134.5
C-12Al-2Ni	0.0028	-266.9	-305.9	0.0011	0.0083	114.9
C-3Al-4Ni	0.0067	-227.7	-264.8	0.0021	0.0087	168.3
C-6Al-4Ni	0.0350	-247.7	-307.7	0.0077	0.0031	84.7
C-9Al-4Ni	0.0035	-222.1	-247.8	0.0012	0.0032	118.6
C-12Al-4Ni	0.0023	-292.0	-295.4	0.0020	0.0110	96.0
C-3Al-6Ni	0.0118	-292.4	-307.6	0.0028	0.0132	137.4
C-6Al-6Ni	0.0310	-267.4	-292.6	0.0072	0.0158	116.5
C-9Al-6Ni	0.0035	-277.7	-295.4	0.0032	0.0060	175.1
C-12Al-6Ni	Rejected					

degree of passivation and, on the other, the lower passive current density ( $I_p$ ) indicated better corrosion resistance. The 9 wt% Al alloys exhibited higher corrosion resistance than the others and demonstrated the easiest passivation.

## DISCUSSION

The available base-metal alloy in dentistry has a much higher modulus of elasticity than the root dentin.<sup>8</sup> The copper alloys have been developed in this study for use as a post and core material. The aimed properties of experimental materials focused upon the mechanical and physical properties of these materials, to be comparable to those of standard, dental gold alloys. Therefore, a desirable value of the elastic modulus of the experimental alloys would be comparable to gold alloys (70-100 GPa), 180 MPa of 0.2% proof strength, and present 10% elongation.

According to the desired properties, Cu-9Al with 2Ni and 4Ni would be most suitable for further investigation. The amount of aluminium added can increase the ultimate tensile strength, 0.2% proof stress, and modulus of elasticity to the optimal level. Adding more aluminium could increase the strength, elastic modulus, and hardness to be much higher than those of tooth structures, which is not beneficial for the intended application. The elongation also decreased when the concentration of aluminium was more than 9%, and the alloy became brittle. The strengthening

effect might be due to the form phase of aluminium with copper, whereby the alloy would form a single-phase (face-centered cubic) alpha alloy, if the alloy containing aluminium contained less than 8%. This alloy has high ductility, and is suitable for cold forming, such as wiring, tubing and sheeting. If the aluminium content was increased to between 8% and 10%, then the alloys were highly strengthened by the appearance of a harder (body-centered cubic) beta phase. This phase made the alloy stronger and more suitable for casting. However, if the aluminium content increased to more than 10%, then it would be difficult to cast, because of the low castability of copper alloy.<sup>15</sup>

The amount of nickel incorporated into the alloy compositions also affected the mechanical and physical properties of the experimental copper alloys, but the effects were not as prominent as those occurring from aluminium. An increase in nickel content of 0 to 4% could not significantly affect the ultimate tensile strength of 3-6 wt% Al alloy (189.4 ± 13.3 to 255.2 ± 25.8 MPa). However, from the static immersion tests, the level of nickel added should not exceed 4%, or the elution of nickel increased. Additionally, the results of the biocompatibility tests showed that the experimental alloys with 6 wt% Ni were more toxic than the other groups.

The 12 wt% Al fusion with 6 wt% Ni could not issue complete castings, and it caused many defects and incomplete castings.

The solidus and liquidus temperatures of all the experimental alloys slightly decreased as the aluminium content increased from 3-12%. The effect of nickel content was not noticeable in this aspect. Thus, the melting ranges were only influenced by the aluminium content. They decreased as the aluminium content increased. The solidus and liquidus temperatures were recorded at circa 1000-1100°C, and therefore within the ranges of commercially available gold alloys.

The ultimate tensile strength and 0.2% proof strength of the experimental alloys exceeded the minimum requirements. The optimum strength required for post and core restoration is crucial, because it has to withstand the complex loading forces which occur during chewing.<sup>16,17</sup> It would be remarkably destructive for the whole restoration, even if a minute amount of deformation occurred along the post and core structure.

The electrochemical behaviors of the experimental alloys showed little difference in the potentiodynamic patterns. Alloys with more aluminium content displayed more stability in the passive film. The aluminium content plays an active role in the corrosion protection of this alloy. Additionally, the formation of a very thin protective film may be due to the characters of these alloys in the 0.9% NaCl electrolyte.<sup>18</sup> The corrosion reaction of copper, especially in a solution containing chloride ions, was quite complicated, but the reactions might briefly be described as the formation of copper (I) cuprous, and copper (II) cupric oxides, together with insoluble hydrated chlorides. Meyer and Nally<sup>19</sup> indicated that 0.9% saline solution was considered to be six times more aggressive than saliva and its artificial substitutes. However, Marek and Topfl<sup>20</sup> suggested that 1% NaCl was unsuitable for measurement, other than the screening test for generalized corrosion.

As a result a slight reduction of corrosion current, tracking on the active peak potential was found. One characteristic of the potentiodynamic polarization curves of the alloys was that they reached their own stable passive current density, and were discovered to be more stable when rising to breakdown potential ( $E_p$ ), which demonstrated the style of their passive behavior.

The electrochemical behaviors of all the experimental alloys can withstand the oxidation potential ranges of the oral cavity<sup>21</sup> (-58 to + 212 mV), due to their passivity potential ( $E_p$ ) remaining stable and within the oral oxidation potential ranges.

The goal of all biocompatibility testing is the screening test for dental materials. ISO standard 7405:2008<sup>22</sup> has suggested a series of tests to ascertain that medical or dental materials, and devices, are biocompatible. This aspect would also include the corrosive behavior of the materials, especially elements released into the simulated environment.

The results of the biocompatibility tests presented moderate cytotoxicity, which was comparable to the positive controls, but lessened in terms of cell response (2/2 and 3/2). Nevertheless, the higher content of nickel exhibited more decolorization zones. The highest content of

nickel, 6 wt % in this study, revealed widespread decolorization zones and, in turn, indicated that nickel had a negative toxicity effect upon the cells. The nickel ion was found to induce the cell to release an intracellular enzyme lactic dehydrogenase, which stimulated lactic acid production. Lactic acid in the cell would cause DNA damage, leading to the response of the cell to repair the DNA.<sup>23</sup> Several studies have shown evidence of the negative effects of nickel in human cells, and numerous nickel compounds are considered to be carcinogens.<sup>24,25</sup> However, more evidence has been found in that nickel contained appliances cause contact allergies. More interestingly, their reactions to dental and orthodontic appliances appear to be infrequent in certain circumstances.<sup>26,27</sup> The results of the biocompatibility presented for the highest content of nickel in this study, 6 wt% Ni, revealed the largest cell response being equal to positive control. For that reason, these alloys were not suitable for application in this situation. However, the element release results showed the lowest levels in the 2 wt% Ni alloys. This would be explained by the reaction of the nickel to aluminum. A small amount of nickel is able to form a completely solidified solution for aluminum, and the rest of the nickel is free in the alloy. However, the total metal ion release (20.3 to 143.9  $\mu\text{g}/\text{cm}^2/7\text{d}$ ) from the experimental alloys into the test solution distributed no greater than the maximum value of the ISO standard specification; not exceeding 200  $\mu\text{g}/\text{cm}^2/7\text{d}$ .<sup>11</sup>

## CONCLUSION

Within the limitations of this study, the following conclusions were drawn:

1. A content of aluminium measured at more than 9% of the experimental alloys exhibited brittleness and low elongation. Once this content reached less than 9% the passive film of these alloys exhibited poor stability, together with the 0.2% proof strength not complying with the ISO standard.
2. Nickel affected the mechanical properties of the experimental alloy less than aluminum did, but clearly influenced the corrosion resistance and stability of the passive film. However, a content of nickel measuring more than 4% in the experimental alloys introduced toxicity equal to positive control.
3. The mechanical properties of the copper alloys fusing of 9 wt% Al and 2-4 wt% Ni complied with the ISO standard. Nevertheless, Cu-9Al-2Ni was considered as a potential material because its properties were in acceptable ranges in both the physical and mechanical properties. Additionally, this alloy presented the least elution of elements when compared with the other groups.

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