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The potential of copper alloy as alternative material for post and core applications

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Abstract

Objective: The purpose of this study was to investigate the use of copper alloy for dental application.

Materials and methods: Three types of copper alloy used in Thailand were selected (Cu-Al, Cu-Al-Ni and Cu-Zn). Ingots of these three alloys were prepared. The tensile test and potentiodynamic polarization for corrosion test were performed following ISO 1562: 2004 Dentistry-Casting gold alloys and ISO 10271: 2001 Dental metallic materials-Corrosion test method. The ultimate strength, 0.2% proof stress, percentage of elongation after fracture and modulus of elasticity were calculated from tensile stress-strain curves. Six specimens for each test were made from each alloy.

Results: The percentage of elongation of Cu-Al, Cu-Al-Ni and Cu-Zn alloys were not significantly different (48.6, 52.1, and 53.3 percent, respectively). The proof stress of Cu-Al and Cu-Al-Ni alloys (88.5 and 72.1 MPa, respectively) were not significantly different, while that of Cu-Zn alloy (38.9 MPa) was the lowest. The ultimate tensile strength of Cu-Al alloy was significantly the highest (321.9 MPa), while that of Cu-Al-Ni and Cu-Zn alloys (207.1 and 215.9 MPa, respectively) were not significantly different. The modulus of elasticity of Cu-Al alloy was significantly the highest (122.9 GPa), while that of Cu-Al-Ni and Cu-Zn alloys (97.9, and 102.3 GPa) were not significantly different. The potentiodynamic curve of Cu-Zn alloy had no passive region, while the curve of Cu-Al alloy had a shorter passive region than that of the Cu-Al-Ni alloy.

Conclusion: Regarding mechanical properties, Cu-Al alloy seemed the most suitable for post and core materials while Cu-Al-Ni alloy had the highest corrosion resistance. Thus, both Cu-Al and Cu-Al-Ni alloys showed promising properties for further development as appropriate post-and-core materials.

Key words: alloy, copper alloy, post and core, Cu-Al alloy, Cu-Al-Ni alloy, Cu-Zn alloy, dental alloy

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Introduction

An ideal post-and-core retained restoration should fail in material composition before damage occurs to the tooth[1] when it has been subjected to abnormal forces such as tooth injuries or bruxing forces. Root fracture of endodontically-treated teeth is a catastrophic failure that requires extraction. There exists a general consensus that endodontically-treated teeth are "more brittle" and more subjected to fracture than vital teeth. Loss of tooth structure, associated with caries, trauma, and restorative and endodontic procedures, is the major factor in weakening the tooth.[2-5] Other possibilities issues are the loss of moisture and changes in properties of the dentin. Moreover some authors[6-7] have implied that dehydration increases brittleness and makes teeth more susceptible to fracture.

Some authors[8-9] have suggested that post materials with moduli of elasticity close to that of the dentine would be less predisposed to induce root fracture than the commonly used metal posts. They believe that when a system with components having different rigidity is loaded, the more rigid component is capable of resisting greater forces without distortion. Stress, therefore, is transferred to the less rigid component which might cause it to fail. It has been suggested that a post should have the modulus of elasticity close to that of the root dentin to distribute applied forces evenly along the length of the post[10-11].

Several studies[12-15] have shown that dehydrated human dentine has an elastic modulus around 17-20 GPa while the closest elastic modulus to that of the dentine is that of gold alloy showing an elastic modulus around 90 GPa[15]. However, this alloy is expensive to use as post and core and its cost continues to increase. Personal communication with several Emeritus Professors revealed information of how the alloys were used in dentistry at the time Thailand was facing with challenging economic situation and alloy crisis period. Copper alloy normally used for minting was then substitute as a dental alloy material. Some properties and colors of that alloy are close to dental gold alloy. However, tarnish and corrosion of that alloy are needed to be investigated.

The aim of this study was to investigate promising copper alloy in develop and use for dental application.

Materials and methods

Three types of copper alloy normally used for minting in Thailand[16] were selected (Cu-Al, Cu-Al-Ni and Cu-Zn). The alloy compositions were provided with courtesy of the Royal Thai Mint, Treasury Department, Ministry of Finance, as shown in Table 1. Ingots of those three alloys were prepared by melting the metal elements in weight percent of each alloy composition in an induction machine (SRF -310W, Tokyo Koshusa-Denkiro, Tokyo, Japan). The tensile properties and potentiodynamic polarization for corrosion test specimens were prepared according to ISO1562: 2004 Dentistry-Casting gold alloys and ISO 10271: 2001 Dental metallic materials-Corrosion test method.

Table 1 The alloy compositions, used in this study

Alloy	Composition (weight percent)			
	Cu	Al	Zn	Ni
Aluminium Bronze (Cu-Al)	91	9		
Nickel Aluminium Bronze (Cu-Al-Ni)	92	6		2
Brass (Cu-Zn)	65		35	

Specimen preparation

Dumbbell shape patterns with a screw thread at the end, size 3 mm in diameter and 42 mm long with 18 mm gauge length for tensile specimens were made by pre-formed acrylic combined with the injection of molten wax into a split-silicone mold.

The squared plated (10mm x 10mm x 2mm) pattern for corrosion test were made by pre-cutting acrylic plate. The tensile and corrosion specimen patterns and their castings were shown in Figure 1. With this technique, consistent dimensions of the specimens were ensured.

Wax patterns for Cu-Al and Cu-Al-Ni alloy were invested in phosphate-bonded investments due to their high melting temperature (casting temperature at 1045°C). Wax patterns for Cu-Zn alloy were produced in gypsum-bonded investment, and then casted by gas air-torched centrifugal casting machine at 920°C. After de-casting, the sprue was carefully separated. The excess nodules or fins were removed using a separating disc and heatless stone bur. Specimens with visible shrinkage defects or porosity were discarded from this study. Six specimens were made from each alloy.

Tensile testing

The tensile properties were measured using the Universal Testing Machine (Instron Model 5566, Instron Corp., Buckinghamshire, UK) at a cross-head speed of 1.5 ± 0.5 mm/min until fracture occurred. The ultimate strength, 0.2% proof stress, percentage of elongation after fracture and modulus of elasticity were calculated from their stress-strain curves.

Corrosion testing

The cast specimens were embedded in cold type epoxy resin size 3 cm in diameter and 1.5 cm in height. The specimens were wet ground with 400 grit, 500 grit and 600 grit silicon carbide paper, respectively using a metallurgical polisher (Pedemax-S, Streuers, Denmark). Prior to testing, the test surface was polished with 6 micrometer and 3 micrometer diamond paste, followed by 0.05 micrometer alumina powder until the alloy showed a mirror-like surface. The specimens were cleaned with an ultrasonic cleanser for two minutes, rinsed with ethanol and dried with oil-free compressed air.

The electrolyte used in this study was 0.9% sodium chloride solution by dissolving 9.0g sodium chloride in 950 ml water. The solution was then adjusted to pH 7.4 ± 0.1 with 4% sodium hydroxide (analytical grade) and diluted to 1000 ml with water.

The electrical potentials were measured with respected to a saturated calomel electrode (SCE). A platinum plate served as a counter electrode and the alloy specimens served as a working electrode. The electrochemical cells

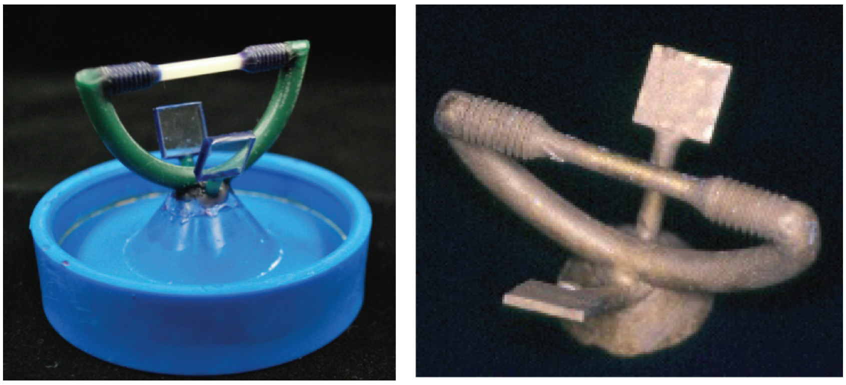

Figure 1 The tensile and corrosion's wax pattern and after alloy casting

were connected to a potentiostat (Model 273A, EG & G Princeton Applied Researcher USA.) and the experiment was controlled by a microcomputer using model 352/252 corrosion analysis software. The open circuit potential versus time and potentiodynamic technique were selected for this study. The complete set up of the electrochemical cell and the polarization system were shown in Figure 2

The open circuit potential (Eocp) was measured versus time for two hours. After that, the potentiodynamic measurement was started at 150 mV lower than Eocp with a scan rate of 1mV/sec. Anodic potential was scanned until reaching the final potential at 1000 mV

The potential and current density were measured and plotted. The value of Eocp (mV, SCE) of each specimen was determined. The characteristic of the anodic curves was evaluated. The value of Ez (zero circuit potential) in mV, SCE; Ec (active peak potential) in mV, SCE ,with corresponding current density Ic in Amps/cm^2, Ep (breakdown potential) in mV and SCE, with corresponding current density Ip in Amps/cm^2, of each specimen were determined. Six specimens of each alloy were run in the same condition. The solution was replaced after each experiment.

The morphology of alloy surfaces before and after electrochemical test was characterized and photographed by scanning electron microscope (JSM-5410LV, JEOL, Japan).

Results

Tensile properties

A summary of tensile properties of three high copper alloys was shown in Table 2. Data in each group were normally distributed and the homogeneity of variances among groups was noted (P>0.05). The result of MANOVA found significant differences (p<0.05) among the three alloys in three properties; 0.2 percent proof stress, ultimate tensile strength and modulus of elasticity, while percentage of

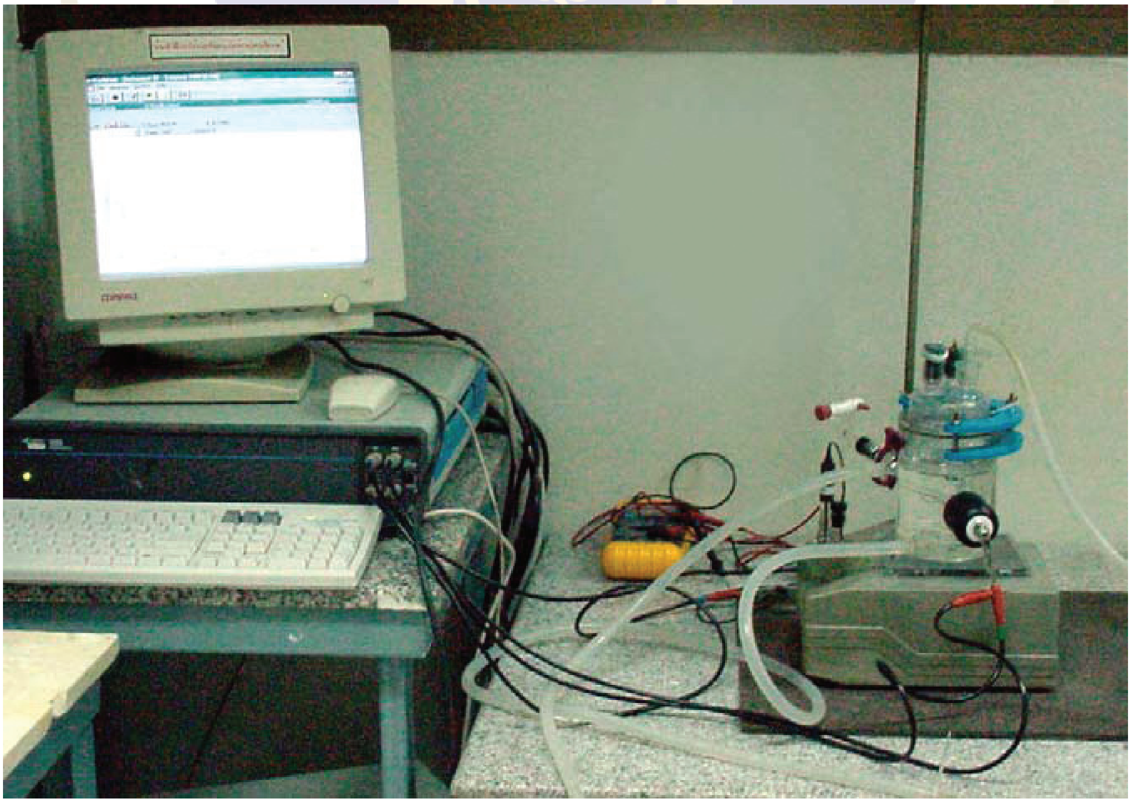

Figure 2 Electrochemical cell and polarization system

elongation was not different statistically ($p>0.05$).

The mean percentage of elongation of Cu-Al, Cu-Al-Ni and Cu-Zn alloys were 48.6, 52.1, and 53.3 percent, respectively. All three alloys had percentages of elongation statistically equal.

The mean 0.2 percent proof stress of Cu-Al, Cu-Al-Ni and Cu-Zn alloys were 88.5, 72.1, and 38.9 MPa, respectively. The mean proof stress of Cu-Al and Cu-Al-Ni alloys were not significantly different, while that of Cu-Zn alloy was lower than the other two alloys.

The mean ultimate tensile strength of Cu-Al, Cu-Al-Ni and Cu-Zn alloys were 321.9, 207.1, and 215.9 MPa, respectively. The mean value of Cu-Al alloy were significantly the highest, while that of Cu-Al-Ni and Cu-Zn alloys were not significantly different.

The mean modulus of elasticity of Cu-Al, Cu-Al-Ni and Cu-Zn alloys were 122.9, 97.9, and 102.3 GPa, respectively. The mean value of Cu-Al alloy was significantly the highest, while that of Cu-Al-Ni and Cu-Zn alloys were not significantly different.

Corrosion resistance

The representative curve of each alloy in the average range with high reproducibility was selected. The curves were overlaid and plotted in the same scale, and were shown in Figure 3. The X-axis of the curve represents the current density (Amps/cm^{2}) and the Y-axis represents the electric potential (Volts). It showed clear polarization characteristic such as changing from cathodic to anodic curve as a sharp transition at a single potential (Ez), the occurrence of Ec with its corresponding Ic, as well as the stability of the film, indicated by the potential of the passive region and the occurrence of Ep with its corresponding Ip. The electrical values of corrosion behavior of the three copper alloys were summarized in Table 3.

Table 2 Mechanical properties of the three copper alloys

	Percentage of elongation (%)	0.2% proof stress (MPa)	Ultimate tensile strength (MPa)	Modulus of elasticity (GPa)
Cu-Al	48.6± 7.0^{a}	88.5± 15.0^{b}	321.9± 20.4^{d}	122.9± 10.9^{f}
Cu-Al-Ni	53.3± 6.8^{a}	72.2± 8.9^{b}	207.1± 23.2^{e}	97.9± 8.4^{g}
Cu-Zn	52.1± 7.7^{a}	38.9± 17.6^{c}	215.9± 16.9^{e}	102.3± 5.5^{g}

* Mean values designated with the same superscript were not significantly different ($P<.05$).

Table 3 Summarized electrical values from polarization curves of the three copper alloys.

	Cu-Al	Cu-Al-Ni	Cu-Zn
Eocp (mV, SCE)	-233	-186	-176
Ez (mV, SCE)	-294	-231	-299
Ic (Amps/cm^{2})	1.61x10^{-2}	1.47x10^{-2}	1.33x10^{-2}
Ec (mV, SCE)	7	77	37
I passivity (Amps/cm^{2})	2.1x10^{-3}	3.3x10^{-3}	8.9x10^{-3}
Passive region (mV, SCE)	105 - 294	200 - 430	no
Ip (Amps/cm^{2})	2.4x10^{-3}	3.0x10^{-3}	8.9x10^{-3}
Ep (mV, SCE)	294	430	127
Corrosion rate (mpy)	2.4x10^{-8}	8.8x10^{-8}	9.7x10^{-7}
Time used to form passive film (seconds)	399	431	356

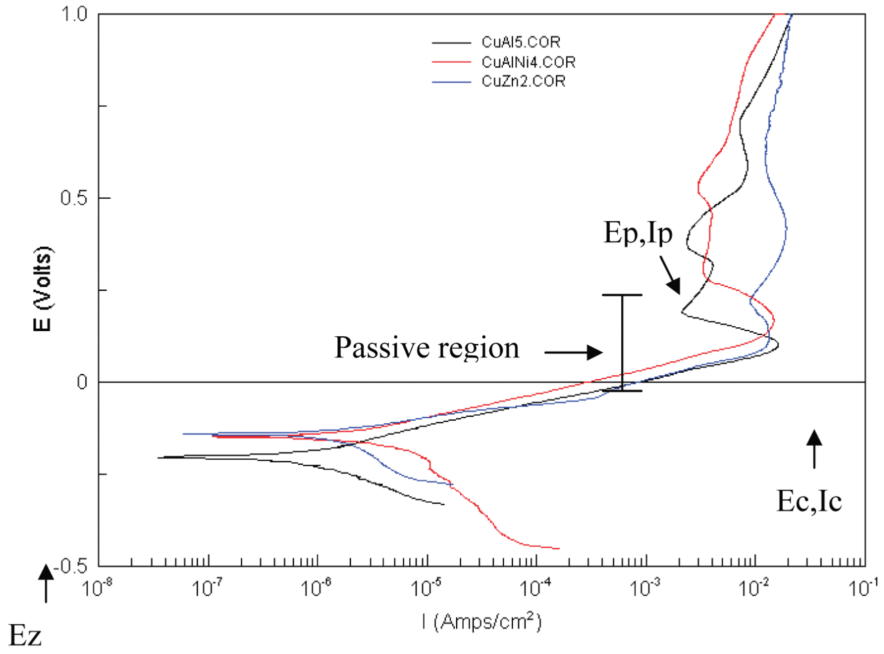

Figure 3 Potentiodynamic polarization curves of three alloys in 37°C de-aerated 0.9% NaCl solution

The mean Eocp of Cu-Al alloy was significantly lower than that of Cu-Al-Ni and Cu-Zn alloy. Surface corrosion products were formed while the specimens were in the anodic regime, i.e., at the zero current potential and upward. We could observe changes in the specimens due to the numerous reactions that occurred as the copper alloys corroded. As the potential was increased between Ez and Ec (see Figure 3), the current density increased sharply and continuously to approximately 0.01 A/cm^2, the value of which was very high. This indicated that the dissolution reaction progressed aggressively and rapidly. When the curves reached the active peak potential (Ec), a small reduction in the corrosion current was observed. The current density of Cu-Al and Cu-Al-Ni alloys were stable in a passive region and then increased again when the curves were increased to the breakdown potential. The curve of Cu-Zn alloy had no passive region because when the potential increased to its breakdown potential (Ep), the current density increased abruptly.

The SEM pictures of the three copper alloys before and after potentiodynamic test are shown in Figure 4. The Cu-Al alloy surface after potentiodynamic test showed numerous corrosion products covering the alloy surfaces with pitting corrosion characteristics. Cu-Al-Ni alloy surface did not show the presence of any localized corrosion characteristics except for the presence of a large grain boundary. While Cu-Zn alloy surface showed crevice corrosion characteristics.

Discussion

According to ISO 1562: 2004 Dentistry-casting gold alloys, the minimum values of percentage elongation after fracture and 0.2 percent proof stress of type III gold alloy are 5% and 270 MPa, respectively. The percentage elongation after fracture and 0.2 percent proof stress of the three copper alloys in this study were about 50% and 38.9-88.5 MPa, respectively. The value of the former was higher than that of the specification while the latter was not acceptable by the specification. The percentage elongation after fracture of these alloys was higher than the specification.

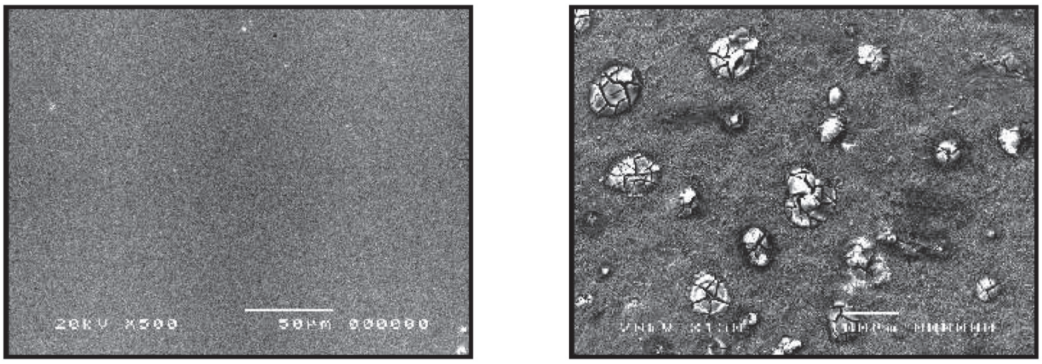

Figure 4-1a **Cu-Al alloy** Figure 4-1b

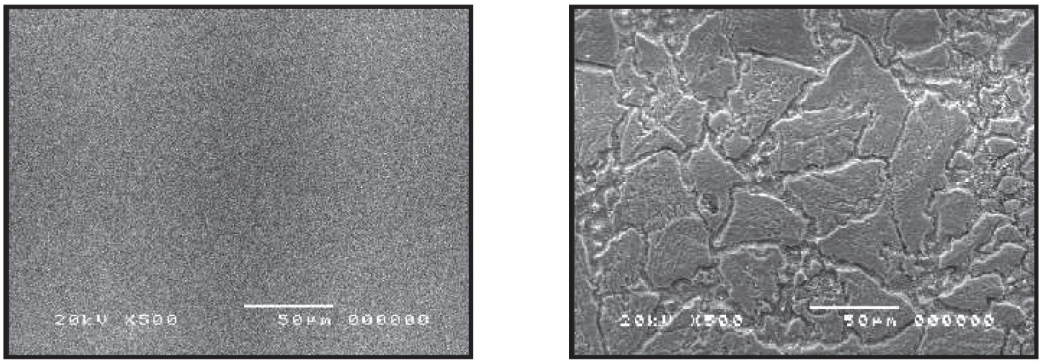

Figure 4-2a **Cu-Al-Ni alloy** Figure 4-2b

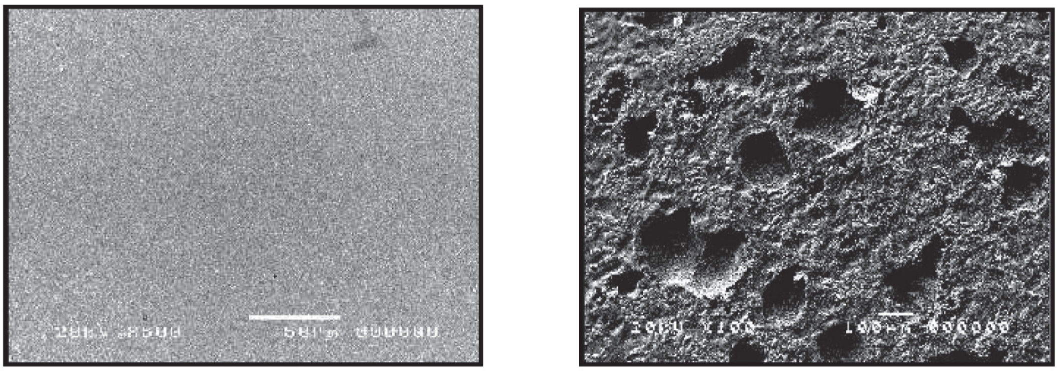

Figure 4-3a **Cu-Zn alloy** Figure 4-3b

Figure 4 Scanning electron micrograph of three alloys before (a) and after (b) potentiodynamic test

The 0.2 percent proof stress and ultimate tensile strength implied to the strength of post-and-core materials. Obviously, post-and-core materials should have high strength to prevent of fracture. ISO specification did not specify the minimum value of ultimate tensile strength, but the ultimate tensile strength of these alloys (207.1-321.9 MPa) was close to that of type I and II gold alloys[17]. The alloys used as post and core materials should have at least an ultimate tensile strength equal to type III gold alloy (421 MPa)[17]. Although these copper alloys had lower proof stress and tensile strength than type III gold alloys, those properties might be improved in future by heat treatment or adding some alloying element, etc.

The moduli of elasticity of three alloys (97.9-122.9 GPa) were close to that of type III gold alloy (100 GPa)[17]. However, these alloys were much cheaper. In this aspect, this value is promising to be developed in further studies because it was not so low a value as that of carbon fiber or glass fiber posts (14-18 GPa)[11,18]. Some researchers[18-19] revealed that occlusal loads may cause the carbon fiber post to flex with eventual micro-movement of the core, and the cement seal at the margin of the crown may fracture in a short time.

The potentiodynamic polarization technique is a fundamental and widely used method for corrosion testing in vitro.

The potentiodynamic curve of Cu-Zn alloy had no passive region. It implied that this alloy had the lowest corrosion resistance among these three alloys. While the curve of Cu-Al alloy had a shorter passive region than that of Cu-Al-Ni alloy and above Ec, its curve looked like a wave because the oxide compounds were oxidized and its protective film changed in structure and composition. Therefore, Cu-Al alloy had lower corrosion resistance than Cu-Al-Ni alloy. The potentiodynamic curve of Cu-Al-Ni alloy had a long passive region. It was hypothesized that Ni is in a transitional element group as Cu, so it goes into solid solution and forms face cubic center phase with Cu if small amounts are added[20].

In this study, we did not quantitatively analyze the change of alloy composition in both specimens and electrolyte after the corrosion resistance test. Hence, we could not identify the structures of any dissolved ion, oxides and chlorides compounds, passive film, or corrosion products. Further studies will be needed to identify the film and clarify the dissolution behavior of these alloys. It should be noted that the formation of oxides and chlorides, and corrosion products of these alloys also affected their microstructures that might degrade some mechanical properties.

Mayer and Nally[21] indicated that 0.9% saline solution was considered to be more aggressive than saliva and its artificial substitutes because the chloride content was six times higher. Moreover, it lacks of some components, which might show a corrosion inhibited action and a buffer capacity such that of phosphate. Marek and Topfl[22] suggested that 1% NaCl was unsuitable for measurement other than the screening test for generalized corrosion. One of the problems associated with the corrosion studies of copper alloys is that knowledge of the electrochemical environment of the oral cavity is limited. This makes the preparation of testing conditions and the interpretation of in vitro data somewhat hypothetical.

The potential that occurred in the oral cavity was reported by Ewers and Greener[23], who produced and developed of electrochemical activity for the oral cavity by collecting data relating to the oxidation potential and pH. They reported the oxidation potential ranged from –58 to +212 mV (SCE) and the pH ranged from 6.1 to 7.9. With regard to the scan conditions in this study, the potential was increased up to 1000mV. The final potential was much higher than the potential that occurred in the oral cavity. Thus, we could not study the corrosion behavior of these alloys under conditions that can occur in the oral cavity. The SEM picture in this study exhibited a severely corroded alloy surface when 0.9% NaCl was used as test media. Such a high potential and corrosive environment caused the copper alloys to corrode aggressively. However, this situation might not occur in the oral cavity. Therefore future research needs to correlate the corrosion behavior of in vitro study with clinical aspects, and should limit the potential to within the range of the oral cavity (-58 to +212 mV).

In conclusion, regarding mechanical

properties, Cu-Al alloy seemed to be the most suitable for post and core material because it had a higher 0.2 percent proof stress and ultimate tensile strength than other two alloys, while for the corrosion resistance test, Cu-Al-Ni alloy had the highest corrosion resistance. Thus, both Cu-Al and Cu-Al-Ni alloys showed promising properties for further development as appropriate post-and-core materials.

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