THE POTENTIAL OF HIGH COPPER ALLOYS AS ALTERNATIVE MATERIALS FOR POST-AND-CORE APPLICATION

USANEE PEUNGPAIBOON

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Usanee Peungpaiboon
....
Miss Usanee Peungpaiboon
Candidate

....
Asst. Prof. Somchai Urapepon,
Ph.D.
Major-advisor

....
Asst. Prof. Widchaya Kanchanavasita,
Ph.D. (Biomaterials)
Co-advisor

....
Assoc. Prof. Rassmidara Hoonsawat
Ph.D.
Dean
Faculty of Graduate Studies

B. Yotneungnut
....
Assoc. Prof. Benjapote Yoteneungnit
Diplomate Thai Board of Prosthodontics
Chair
Master of Science Programme in Prosthodontics
Faculty of Dentistry

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on
26 May, 2004

Miss Usanee Peungpaiboon
Candidate

Asst. Prof. Somchai Urapepon,
Ph.D.
Chair

Asst. Prof. Widchaya Kanchanavasita,
Ph.D. (Biomaterials)
Thesis Defense Committee

Mr. Jintamai Suwanprateeb
Ph.D. (Biomaterials)
Thesis Defense Committee

Mr. Julathep Kajornchaiyakul
Ph.D.(Metallurgical and Materials Engineering)
Thesis Defense Committee

Assoc. Prof. Rassmidara Hoonsawat
Ph.D.
Dean
Faculty of Graduate Studies
Mahidol University

Assoc. Prof. Jurai Nakaparksin
MS.
Dean
Faculty of Dentistry
Mahidol University

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Usanee Peungpaiboon

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USANEE PEUNGPAIBOON 4336389 DTPT/M

M.Sc. (PROSTHODONTICS)

THESIS ADVISORS : SOMCHAI URAPEPON, Ph.D., WIDCHAYA KANCHANAVASITA, Ph.D.

ABSTRACT

The purposes of this study are to compare mechanical properties and corrosion resistance of three copper alloys (CuAl, CuAlNi, CuZn), and to determine the potential of these alloys for further development as post-and-core materials. Six tensile bars and six square plated specimens of each alloy were prepared and tested according to ISO1562 for mechanical properties and ISO 10271 for corrosion resistance. 0.2 percent proof stress, modulus of elasticity, percentage elongation after fracture, and tensile strength were calculated from load-displacement curve obtained from the record chart of the Universal Testing Machine (UTM). One way ANOVA and Tukey HSD were used to determine the difference in properties among the alloys. Potentiodynamic technique was selected to test the corrosion resistance of the alloys. The test was performed in 37ºc de-aerated 0.9% NaCl solution. The characteristics of the potentiodynamic curve of each alloy were compared.

All alloys were not different in percentage elongation, while 0.2 percent proof stress and ultimate tensile strength of CuAl was significantly higher than those of CuAlNi and CuZn. Although the moduli of elasticity value were not valid in this study, a pilot study showed a promising value suitable for post-and-core application. Only 0.2 percent proof stress and ultimate tensile strength were not satisfying as criteria for a good post and core material. Potentiodynamic curves of CuAlNi showed a longer passive region than that of CuAl, while that of CuZn did not show any passive region. In conclusion, CuAl and CuAlNi alloys have a potential for further development as good post-and-core materials.

KEY WORDS : COPPER ALLOYS/ POST-AND-CORE/ MECHANICAL
PROPERTIES/ CORROSION RESISTANCE

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ศักยภาพของโลหะเจือทองแดงเพื่อใช้เป็นวัสดุทางเลือกสำหรับทำเดือยฟัน (THE POTENTIAL OF HIGH COPPER ALLOYS AS ALTERNATIVE MATERIALS FOR POST-AND-CORE APPLICATION)

อุษณีย์ ปึงไพบูลย์ 4336389 DTPT/M

วท.ม. (ทันตกรรมประดิษฐ์)

คณะกรรมการควบคุมวิทยานิพนธ์ : สมชาย อุรพีพล, Ph.D., วิชญ กาญจนะวสิต, Ph.D.

บทคัดย่อ

การศึกษานี้มีวัตถุประสงค์เพื่อเปรียบเทียบสมบัติเชิงกลและความต้านทานการกัดกร่อนของโลหะเจือทองแดง 3 ชนิด (CuAl, CuAlNi, CuZn) และเพื่อประเมินความเป็นไปได้ในการพัฒนาเป็นวัสดุทำเดือยฟัน เตรียมชิ้นตัวอย่างจากโลหะเจือแต่ละชนิด 6 ชิ้นตามข้อกำหนดของ ISO 1562 เพื่อทดสอบสมบัติเชิงกลและอีก 6 ชิ้นตามข้อกำหนดของ ISO 10271 เพื่อทดสอบความต้านทานการกัดกร่อน คำนวณค่าความเค้นพิสูจน์ร้อยละ 0.2, มอดุลัสของสภาพยืดหยุ่น, ร้อยละของการยืดภายหลังการแตกหักและความต้านแรงดึงจากกราฟระหว่างแรงและระยะทางของเครื่องทดสอบสากล วิเคราะห์หาความแตกต่างระหว่างข้อมูลที่คำนวณได้โดยใช้สถิติวิเคราะห์ความแปรปรวนแบบทางเดียวและ Tukey HSD ทดสอบความต้านทานการกัดกร่อนโดยใช้เทคนิค Potentiodynamic ในสารละลายน้ำเกลือความเข้มข้นร้อยละ0.9ในภาวะปราศจากแก๊สออกซิเจนที่อุณหภูมิ 37 องศาเซลเซียส เปรียบเทียบลักษณะของกราฟ Potentiodynamic ระหว่างโลหะเจือแต่ละชนิด

ร้อยละของการยืดภายหลังการแตกหักไม่มีความแตกต่างกันอย่างมีนัยสำคัญทางสถิติ ขณะที่ความเค้นพิสูจน์ร้อยละ0.2 และความต้านแรงดึงของ CuAl มีค่าสูงกว่า CuAlNiและCuZn อย่างมีนัยสำคัญ ถึงแม้ว่าในการศึกษานี้จะไม่สามารถหาค่ามอดุลัสของสภาพยืดหยุ่นได้ แต่ในการศึกษานำร่องแสดงค่ามอดุลัสของสภาพยืดหยุ่นที่เหมาะสมกับการพัฒนาเพื่อใช้ทำเดือยฟัน มีเพียงความเค้นพิสูจน์ร้อยละ0.2 และความต้านแรงดึงที่ไม่ผ่านการประเมินตามข้อกำหนดของวัสดุทำเดือยฟัน กราฟ Potentiodynamic ของCuAlNi มีสภาพ passive คงอยู่ยาวนานกว่า CuAl ขณะที่กราฟของ CuZn ไม่พบสภาพ passive โดยสรุป CuAl และ CuAlNi มีศักยภาพที่จะพัฒนาต่อไปในอนาคตเพื่อใช้เป็นวัสดุในการทำเดือยฟัน

31 หน้า ISBN 974-04-4943-3

CONTENTS

CHAPTER

LIST OF TABLES

LIST OF FIGURES

Figure Page

CHAPTER 1
INTRODUCTION

An ideal post-and-core retained restoration should fail in material part 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 has been 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, restorative and endodontic procedures is the major factor in weakening the tooth (2,3,4,5). Other possibilities that still have been controversial issues are loss of moisture and changes in properties of dentin.

Some authors (6,7) have implied that dehydration increases brittleness and makes teeth more susceptible to fracture. However, Huang et al. (8) indicated that dehydration does not appear to weaken dentin structure in terms of strength and toughness. Some reports (9,10,11) have shown that there is a difference in properties of dentin between endodontically treated teeth and vital teeth, while other reports (4,8,12) revealed no differences in modulus of elasticity, proportional limit, and strength.

Furthermore, some authors (13,14) suggested that post materials with moduli of elasticity close to that of dentine would be less predisposed to induce root fracture than the commonly used metal posts. They believed that when a system with components of different rigidity is loaded, the more rigid component is capable of resisting greater forces without distortion. Stress is therefore transferred to the less rigid component which might cause it to fail.

The literature (15,16,17,18) also reported that electrochemical reaction of metallic post-and-core material could cause root fracture. Silness et al. (18) have proposed that the corrosion products often migrate into the adjacent dentinal tubules, obliterating them and gradually building up intratubular pressures. These pressures may exceed the strength of the root itself, resulting in root fractures. The corrosion products then continue to migrate into the periodontal space, leading to periodontal complications.

Two systems available for constructing post-and-core restoration are (1) the conventional post-and-core cast as a single unit; and (2) a post with core build-up, in which prefabricated commercial post of various designs is built up with core of various materials. At the present time, there are no specific requirements for alloys used as post-and-core material, but gold alloys have been used many years. So, in our study, we used ISO/FDIS 1562:2003(E) Dentistry-casting gold alloys and 10271:2001 (E) Dental metallic materials-corrosion test method as requirements for evaluation of these alloys.

The alloys used for casting post-and-core must exhibit biocompatibility, ease of melting and casting, low solidification shrinkage, high strength, and excellent corrosion resistance. Furthermore, it has been suggested that a post should have the modulus of elasticity close to that of root dentin to distribute applied forces evenly along the length of post (19,20).

Although the elastic modulus of the post was comparable to human dentin, this property will not ensure similar clinical behavior for the post and radicular dentin (21,22). The root is essentially a hollow tube, and the thin rod-shaped post is within this hollow tube surrounded by an interventing layer of luting agent. The radically different configuration of the root compared with the post combined with the interposed luting material suggests that the flexibility of the post will not match the flexibility of the root. A flexible post can be detrimental especially when there is little remaining natural tooth structure between the margin of the core and the gingival extension of the artificial crown. When the ferrule is absent or extremely small, occlusal loads may cause the post to flex with eventual micromovement of the core, and the cement seal at the margin of the crown may fracture in a short time.

Alloys normally used for casting post-and-core:

	Type	Modulus of elasticity (GPa) (23)
1.	Type III, IV gold alloy	95-108
2.	Palladium-based alloy	103-134

3.	Silver-Palladium alloy	99-117
4.	Nickel-Chromium alloy	145-171

In general, the modulus of elasticity of nickel-chromium alloys is approximately twice that of gold alloys and silver-palladium alloys. In addition to the alloys mentioned above, aluminum bronze alloys used as material for crown, bridge and partial denture framework have been approved by the ADA. It may contain between 81 to 88 wt % copper, 7 to 11 wt % aluminum, 2 to 4 wt % nickel, and 1 to 4 wt % iron. Few clinical data are available for this type of alloy.

Aluminum bronzes are used widely for bushings and bearings in light and high-speed work, valve guides, rolling-mill bearings, screwdown nuts slippers and in precision machines. They show good mechanical properties and high corrosion resistance. Moreover, our pilot study of some copper alloys revealed that their elastic modulus is close to that of dentin. Therefore, these alloys may have a potential to be developed as the alloys used for post-and-core application.

Objective

The purpose of this study was

1. To compare percentage of elongation after fracture, 0.2 percent proof stress, tensile strength, modulus of elasticity and corrosion resistance among three high copper alloys (CuAl, CuAlNi, CuZn).
2. To determine whether the properties mentioned in 1 for each alloy satisfied the requirements for alloys used as post-and-core material.

Research hypotheses

1. There was no significant difference of percentage of elongation after fracture, 0.2 percent proof stress, tensile strength, modulus of elasticity and corrosion resistance among three high copper alloys.
2. Percentage of elongation after fracture, 0.2 percent proof stress, tensile strength, modulus of elasticity and corrosion resistance of each alloy satisfied ISO No.1562 and 10271 requirements.

Statistical analysis

1. H_0: The mean 0.2% proof stress of 3 copper alloys were equal.
   [H_0: $\mu_{ps1} = \mu_{ps2} = \mu_{ps3}$ where μ_{ps} was the mean 0.2% proof stress.]
   H_1: At least the mean 0.2% proof stress of 1 pair of copper alloy was different.
2. H_0: The mean modulus of elasticity of 3 copper alloys were equal.
   [H_0: $\mu_{E1} = \mu_{E2} = \mu_{E3}$ where μ_E was the mean modulus of elasticity.]
   H_1: At least the modulus of elasticity of 1 pair of copper alloy was different.
3. H_0: The mean percentage elongation after fracture of 3 copper alloys were equal.
   [H_0: $\mu_{pl1} = \mu_{pl2} = \mu_{pl3}$ where μ_{pl} was the mean percentage elongation after fracture.]
   H_1: At least the percentage elongation after fracture of 1 pair of copper alloy was different.
4. H_0: The mean tensile strength of 3 copper alloys were equal.
   [H_0: $\mu_{ts1} = \mu_{ts2} = \mu_{ts3}$ where μ_{ts} was the mean tensile strength.]
   H_1: At least the mean tensile strength of 1 pair of copper alloy was different.
5. H_0: The means open circuit potential of 3 copper alloys were equal.
   [H_0: $\mu_{Eocp1} = \mu_{Eocp\,2} = \mu_{Eocp\,3}$ where μ_{Eocp} was the mean open circuit potential.]
   H_1: At least the mean open circuit potential of 1 pair of copper alloy was different.

CHAPTER 2

LITERATURE REVIEW

Alloys used for casting post-and-core can be classified into three groups.

- Gold and palladium alloys

In the 1950s selection of an alloy for a cast metal restoration would simply have entailed choosing ADA approved high gold alloys, all of which had a more than 75% gold and platinum content. The soft type I alloys contained at least 83% of noble metals whereas harder alloys (types II, III and IV) contain a larger amount of silver and copper. Type I alloys were used for small inlays, type II for large inlays, type III for post-and-core, crowns and bridges, and type IV for partial denture frameworks.

In the early 1970s, the gold price increased four folds, resulting in the introduction of less expensive alloys with lower noble metal content. Palladium, which had been used since the 1930s to produce a cheaper white gold (Au 30%, Pd 10-35%, Ag 35-60%, Cu 6-25%), became the noble constituent of many of the recent commercial alloys. These alloys include:

- Silver-palladium
- Palladium-silver-gold
- Gold-silver-copper-palladium (with a gold content greater than 40%)
- Palladium-copper
- Palladium-tin

Palladium has a strong whitening effect, which means that most of these alloys will have a silvery appearance unless the gold content is greater than 40% and the palladium less than 6%. Unfortunately, both palladium and silver absorb oxygen when molten, which can result in porous castings especially if casting buttons are reused. Also, reducing the gold content lowers the specific gravity (density), which may make casting less reliable than high gold alloys. This is because less dense alloys have lower kinetic energy during casting, which in turn reduces the penetration of molten metal into the mould. Nevertheless, some authorities argue that with ideal conditions almost all commercial alloys result in acceptable castings (24), but experience indicates that technicians may find such conditions difficult to achieve.

Tarnishing of some alloys is noticeable in certain patients, particularly around the margins of their restorations. This observation is born out by a five-year clinical study comparing two palladium-silver alloys to a type III alloy (25). In the UK the National Health Service has encouraged the use of alloys containing only 30% gold. The potential for corrosion problems to result from this change is currently unknown.

Allergies to gold, palladium and platinum are extremely rare (26). In-vitro studies (27) showed that high gold alloys have excellent corrosion resistance, which implies that few metal ions eluted from restorations. Metal ions are eluted more easily from alloys of low noble metal content, including those containing copper and silver. Copper ions have been implicated in producing lichenoid reactions (28). However, lichenoid reactions to metal ions from crowns, are not as well described as for amalgam where many lichen planus series show up to a third of patients to be sensitive to mercury salts. This raises the possibility that some cases of lichen planus adjacent to crowns may be linked to the underlying amalgam core. Nevertheless, with current trends to use more easily corrosive casting alloys we should be alert to the possibility of more lichen reactions in the future.

- Base metal alloys

Base metal alloys used to make indirect restorations include:

- Nickel-chromium
- Nickel-chromium-beryllium
- Titanium
- Copper-based

- Nickel-chromium alloys

The most commonly used base metal alloys are nickel-chromium and nickel-chromium-beryllium. Beryllium is added to improve the alloy’s physical properties; it is used as a hardener and grain structure refiner and to reduce the alloy’s fusion temperature. As a result of health concerns molybdenum is added to some alloys instead of beryllium. All of these alloys have a higher modulus of elasticity than noble alloys. This means that they are more rigid, which is helpful in preventing flexure of long-span bridges. Rigidity in thin section is necessary for adhesive bridge frameworks and for adhesively-retianed shims used to restore the palatal surfaces of worn incisors.

In general, nickel alloys without beryllium demonstrate poorer castability than those containing up to 1.8 wt % beryllium. The subject of castability is controversial because some researchers claim that alloys theoretically produce complete castings under optimum burnout, melting, and casting conditions. However, the generalized statements on the superiority of beryllium or nonberyllium alloys should not be made without appropriate supporting research data and statistical analysis(29).

Nickel allergy incidence for all age groups was 4.5% for women and 1.5% for men (29). Of the positive reactions to nickel, women with pierced ears accounted for 90% of the total. None of the males with pierced ears exhibited positive reactions. No correlation was found between the incidence of nickel hypersensitivity and the presence of nickel alloys restorations intra-orally.

- Titanium

Titanium and its alloys are well known for biocompatibility. Restorations can be either cast or electro-formed. Casting required high temperatures (1650 °C) and a special magnesium investment. Titanium oxidises easily, so an argon arc is used to melt the metal and casting is performed under vacumm. In 1985, Ida et al (30) reported that the fit of cast titanium crowns was intermediate between those made from a high noble alloy and nickel-chromium alloys. Electro-forming was introduced in 1989 and involves the milling of a titanium blank by spark erosion. A two-year clinical follow-up of electro-formed copings veneered with composite have shown encouraging results.

- Copper-based alloys

The search for an alternative to conventional gold alloy has been carried out for many decades. To avoid bending or breaking of post, the alloy chosen should have relatively high proportional limit and tensile strength. Occasionally, cost considerations drive the selection of the cheapest alloy, however corrosion and problems with castability should always be born in mind; porosity within a cast post can often result in post fracture with unfortunate consequences and thin posts are more likely to suffer critical porosity than thicker ones.

Copper-based alloys, which contain mainly copper and zinc, and bronzes, primarily consisting of copper and aluminum, had been two types of copper-based alloys used for casting restoration and prostheses e.g. crown, prefabricated post, and removable partial denture skeleton. In general, they exhibit good mechanical properties, which can often be varied by heat treatment. Unfortunately, properties, such as hardness and strength, are often achieved at the expense of corrosion resistance. Copper-aluminum alloys were developed primarily for marine use, for which their corrosion resistant properties are of considerable importance (31). These alloys have variable compositions of the basic elements as well as secondary elements, such as nickel, iron, manganese, silicon, phosphorus, etc.

In 1973 Ismail and Lyon (32) suggested that Progold®, a copper-zinc alloy, should be used for inlay, crown and short span bridge. It demonstrated acceptable corrosion resistance, physical properties and tissue compatibility (33). Tarnish resistance of this alloy had been evaluated previously by visual examination of cast samples exposed to ammonium sulfide vapor (32). It had been reported that Progold® maintained a permanent brilliant gold color in the mouth, thereby indicating that the in vivo corrosion resistance of this alloy is satisfactory.

Geissler (34) investigated an aluminum bronze, known as Nikallium® to establish its suitability as a denture base material cast with integral clasps. He found its hardness, ultimate tensile strength and modulus of elasticity to be similar to the gold alloys but it had lower modulus of elasticity and higher percentage of elongation than those of cobalt-chromium.

The main problem of using copper alloys in some clinical situation is their low corrosion resistance (35,36,37,38,39). Some authors revealed that the cause of this problem was due to a preferential dissolution of zinc and aluminum (40,41,42).

Some researcher tried to increase corrosion resistance of copper-based alloy by electroplating gold on to the Nikallium® and Dentatus® screw post, a copper-zinc alloy (35,43). However, some authors indicated that the gold layer deposited on the post does not block the corrosion process (44,45) because the pure gold layer tend to wear quickly (35). In 1973 Britton suggested that tin-nickel-electrodeposited alloy might form a suitable protective layer over Nikallium® for intra-oral application.

Murray (46) founded that the use of tin-nickel alloy plated on aluminum bronze partial denture castings are promising as an effective deterrent to corrosion.

Another method to improve corrosion resistance of copper-based alloy was available in 1991. Guastaldi et al (36) concluded that heat treatment substantially changed its microstructure and improved its corrosion resistance of copper-based alloys.

CHAPTER 3

MATERIALS AND METHODS

Materials and equipments

1.Three high copper alloys (47) used in this study were

Alloy	Composition (wt%)			
	Cu	**Al**	**Zn**	**Ni**
1). **Aluminum bronze (CuAl)**	91	9		
2). **Nickel aluminum bronze (CuAlNi)**	92	6		2
3). **Copper-Zinc base (CuZn)**	65		35	

2.Plastic bars ∅ 3.0 mm

3.Injecting wax

4.Silicone mold for wax injection

5.Plastic sheet (10mm x 10mm x 2mm)

6.Spruing wax ∅ 2mm, 4mm

7.Debulbilizing agent

8.Casting ring ∅ 3 inches and crucible former

9.Absorbent lining paper size 91

10.Phosphate-bonded investment

11.Gypsum-bonded investment

12.Induction machine (Microtonic, Schutz-Dental, Germany)

13.Centrifugal casting machine

14.Carborundum disc

15.Sandblasting device with aluminum oxide 50 µm

16.200-, 400-, 600-, 800- and 1000-grit silicon carbide paper

17.Metallographic Polisher with 1 μm diamond paste (METASERV 2000, Buchler UK LTD., England.)
18.Universal Testing Machine (INSTRON 5566, INSTRON LTD., England.)
19.Metallurgical Microscopes (Olympus Model BHM, Olympus Optical CO., LTD.)
20. Scanning electron microscope (model 5410LV, JEOL, Japan)
21.Materials and equipment for potentiodynamic polarization test

Methods

Mechanical properties and corrosion resistance of 3 types of high copper alloys evaluated in this study were

1.0.2 percent proof stress
2.Modulus of elasticity
3.Percentage elongation after fracture
4.Tensile strength
5.Potentiodynamic polarization test

1. 0.2 percent proof stress, modulus of elasticity, percentage elongation after fracture and tensile strength were determined using tensile specimens (Figure 3-1). The wax patterns were made by injection of molten wax into a split-silicone mold so that consistent dimensions was ensured. The sprue system was shown in Figure 3-2. Wax patterns for CuAl and CuAlNi were invested in phosphate-bonded investments. Their molds were placed in the cradle of the induction machine to align the long axis of tensile specimens with the plane of rotation of the machine and then cast at 1045°c.

Wax patterns for CuZn alloy were invested in gypsum-bonded investment, and burned out at 700°c. Then they were cast by gas torched centrifugal casting machine at 920°c. Flux was used during the casting procedure.

The amount of each alloy used (25 to 26 grams) was sufficient to fill the mold without forming the button. These sprues were carefully separated and any nodules or fins were removed using separating disc and heatless stone bur. Any specimens with visible shrinkage defects or porosity were discarded. Six specimens were made from each alloy.

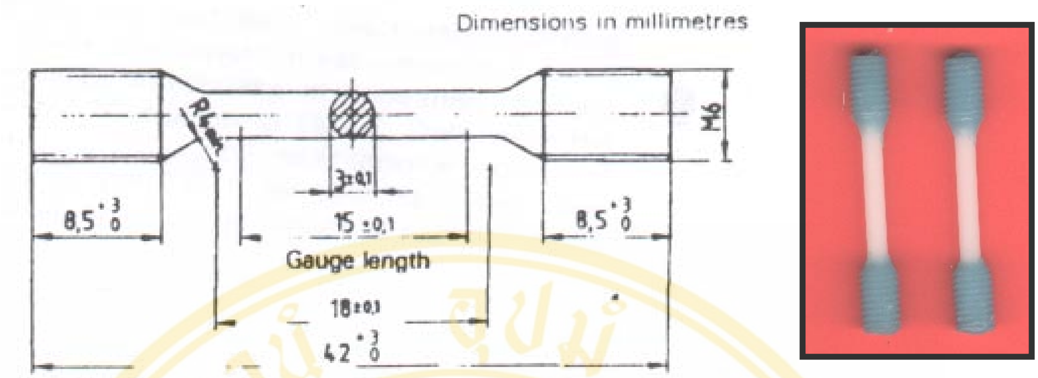

Figure 3-1. Test specimens with threaded ends

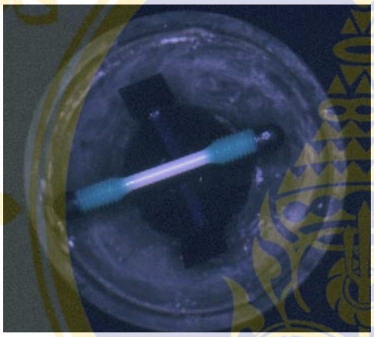

Figure 3-2a

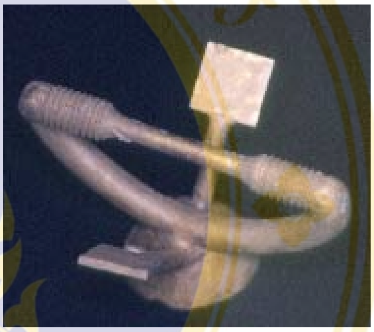

Figure 3-2b

Figure 3-2a. Wax pattern of test specimen with sprues and sprue button

Figure 3-2b Casting of specimen for mechanical properties test and corrosion resistance test.

The mechanical properties of the specimens were measured using the Instron Testing Machine at a cross-head speed of 1.5 ± 0.5 mm/min until fracture occured. Data at the 0.2 % offset level was calculated from the load-displacement curve obtained on the chart paper print out.

2. Corrosion resistance test

2.1 Specimen for electrochemical test

Six squared plated (10mm x 10mm x 2mm) specimens were prepared from each alloy (Figure 3-3). Eighteen specimens were prepared for this study

1. The specimen was placed at the center of the lubricated plaster mold (3 cm in diameter, 1.5 cm in height). A cold epoxy resin was poured to the mold until the top of specimen was covered. The mold was then stored at 37±1°C for 24 hours.

2. The epoxy resin block was removed and both surfaces were wet ground with 400 grit silicon carbide paper (SiC) until the surfaces were exposed. The test surface were then wet ground with 500 grit SiC for 30 seconds, followed by 600 grit SiC for 60 seconds using metallurgical polisher (model Pedemax-S, Streuers, Denmark) under a 100 N load.
3. Prior to testing, the test surface was polished with 6 µm and 3 µm diamond paste, followed by 0.05 µm alumina powder. The surface was cleaned with ultrasonic cleanser for 2 minutes in distilled water. Then it was rinsed with ethanol and dried with oil and water-free compressed air (Figure 3-4).
4. The polished surface was evaluated by metallurgical microscope (x40, model optiphot2, Nikon, Japan). There were neither scratches on the test surface nor the space between specimen and epoxy. The surface area exposed to the test solution was 1 cm^2 for each specimen.

Figure 3-3 specimens before polishing

Figure 3-4 specimen after polishing

2.2 Electrolyte

The electrolyte used in this study was 0.9% sodium chloride solution. Chemical compositions of this solution were

1.Sodium chloride (NaCl), analytical grade
2.Sodium hydroxide (NaOH) , analytical grade
3.Water, complying with grade 2 of ISO 3696:1987
4.Nitrogen gas, with oxygen content $\leq 5X10^{-6}$

2.3 Electrolyte preparation

9.0 g NaCl was dissolved in 950ml water. Then it was adjusted to pH 7.4 ± 0.1 with 4% NaOH, analytical grade and diluted to 1000 ml. with water.

2.4 Electrochemical cell and the polarization system

The electrochemical cell was shown in Figure 3-5.

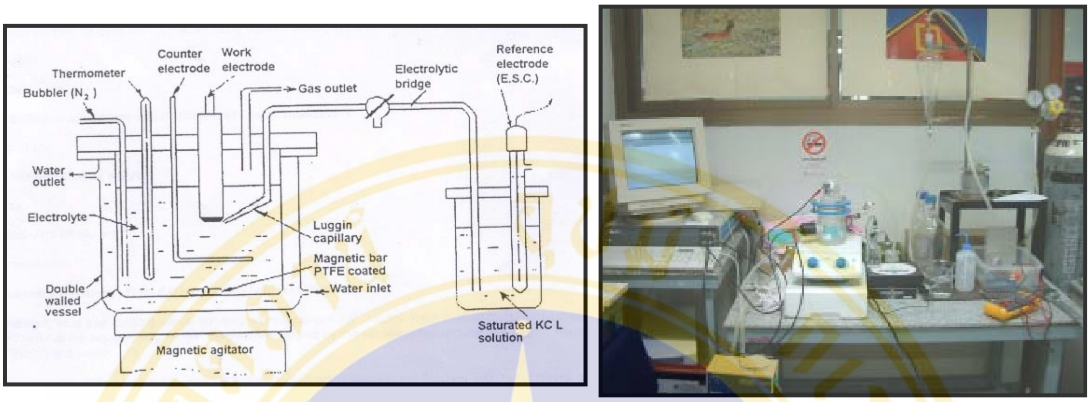

Figure 3-5. Schematic of electrochemical cell

It composed of two closed glass flask with an outer jacket for temperature control with water flow and necks to permit the inlet of working electrode, counter electrode, reference electrode, gas inlet and outlet tubes and a thermometer. The inlet of working electrode was located at the middle part of the flask, where the sample holder was attached to. All electrical potentials were measured with respect 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 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.

2.5 The measurement of potentiodynamic anodic polarization:

1. The epoxy resin block was placed inside the sample holder and assembled together. One end of the alloy specimen was exposed to the electrolyte solution used for corrosion testing and the other end which attached to stainless steel plate was painted with silver paint to improve electric contact. The holder was screwed into the inlet of the working electrode.
2. One liter of test solution was transferred to the prepared electrochemical cell and the temperature controlling device was adjusted to bring the temperature of solution up to 37±1°C. Then the electrolyte was transferred to the test cell.
3. The counter electrode and reference electrode were placed in the test cell. Then the working electrode was placed in the test cell without immersion. The magnetic stirrer

was activated. Oxygen-free nitrogen gas was bubbled at a rate of about 100 cm^3/min through the electrolyte for 30 minutes. The working electrode was immersed in the electrolyte. The gas flow rate was adjusted to give a slight bubbling.

3. When the sample was completely immersed in the solution, the potentiostat was turned on and the software was started. The open circuit potential VS time and potentiodynamic technique was selected for this study.

4. The open circuit potential (Eocp) was measured versus time for 2 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 electrode and scanning conditions were summarized in Table3-1.

Table 3-1. Electrode and scan conditions.

Counter electrode:	Platinum
Reference electrode:	Ag/AgCl
Working electrode :	Alloy specimen
Scan range :	-150 vs. Eocp to 1000 mV
Scan rate:	1 mV /sec
Temperature:	37±1°C

5. The potential and the log of 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 A/cm^2; Ep (breakdown potential) in mV,SCE, with corresponding current density Ip in A/cm^2 of each specimen were determined.

6 The specimen was removed from of electrochemical cell and the test cell was rinsed with distilled water. Six specimens of each alloy were run in the same condition. The solution was replaced after each experiment.

7. The morphology and composition of alloy surfaces after electrochemical test was characterized and photographed by SEM (model 5410LV, JEOL, Japan). Then the results were compared with surface of specimens which were not subject to corrosion test.

Data analysis

The data received from these tests were analyzed to

1. compare mechanical properties and corrosion resistance of three different alloys.
2. compare mechanical properties and corrosion resistance of each alloy according to the ISO 1562, 10271 requirements.

Statistical analysis

The test statistic used in this study was one-way ANOVA and Tukey HSD multiple comparison test. One-way ANOVA was used to compare the mechanical properties and open circuit potential of each alloy due to

1. The data in each group were normally distributed, as proven by Kolmogorov Smirnov test.
2. Each group of samples was independent.
3. The variances of each group were not different, as proven by Levene’s test.

CHAPTER 4

RESULTS

Part I

A summary of mechanical properties of three high copper alloys was shown in Table 4-1. Data in each group were normally distributed and homogeneity of variances among groups was noted, therefore one way ANOVA were chosen for statistical analysis of mechanical properties data. A Tukey HSD Multiple comparison test was used to find out which mean differed from one another if the computed value of F statistic in one way ANOVA was significant.

The mean percentage elongation of CuAl, CuAlNi and CuZn were 53.2, 51.1, and 52.2, respectively. One way ANOVA showed that the mean values of the three copper alloys were not significantly different. This would imply that percentage elongation of these alloys was not affected by the type of alloys.

The mean 0.2 percent proof stress of CuAl, CuAlNi and CuZn were 92.2, 71.9, and 38.9 MPa, respectively. One way ANOVA showed that the mean values of the three copper alloys were significant different. Tukey HSD Multiple comparison test showed that the mean value of CuAl was significantly higher than that of CuAlNi and CuZn, respectively

The mean ultimate tensile strength of CuAl, CuAlNi and CuZn were 322.9, 206.7, and 215.9 MPa, respectively. One way ANOVA showed that the mean values of the three copper alloys were significant different. Tukey HSD Multiple comparison test showed that the mean value of CuAl were significantly highest, while that of CuAlNi and CuZn were not significantly different.

From statistical analysis, only 0.2 percent proof stress and ultimate tensile strength were affected by the type of alloys.

The modulus of elasticity of three copper alloys was not reported due to some error during attachment of the extensometer to the specimens.

Table 4-1 Mechanical properties of three copper alloys

Type	Percentage of elongation			0.2 percent proof stress (MPa)			Ultimate tensile strength (MPa)		
	Min.	Max.	Mean (S.D)	Min.	Max.	Mean (S.D)	Min.	Max.	Mean (S.D)
CuAl	39.7	72.6	53.2^{a} (11.7)	82.1	105.4	92.2^{b} (8.7)	307.3	355	322.9^{e} (19.4)
CuAlNi	43.3	63.7	51.1^{a} (7.7)	63.7	82.1	71.9^{c} (8.6)	185.9	245.6	206.7^{f} (22.4)
CuZn	40.5	59.9	52.2^{a} (7.7)	20.5	69.3	38.9^{d} (17.6)	194.2	233.6	215.9^{f} (16.9)

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

Part II

The mean values of open circuit potential (Eocp) were summarized in Table 4-2. One curve of each alloy in the average range which high reproducibility was selected as a representative curve. It showed clear characteristic such as changing from cathodic to anodic curve as sharp transition at a single potential (Ez), the occurrence of Ec with its corresponding Ic, as well as the stability of the film which indicated by the potential of the passive region and the occurrence of Ep with its corresponding Ip. The corrosion behavior of three copper alloys could be summarized in Table 4-3. Figure 4-1 showed the representative curves of three alloys which were overlaid and plotted in the same scale. The X-axis of the curve was the current density (Amps/cm^2) and the Y-axis was the electric potential (Volts, SCE).

Table 4-2 Mean (S.D.) of Eocp of three copper alloys

Eocp (mV,SCE)	
Alloy	**Mean (S.D.)**
CuAl	-233^{a} (19.58)
CuAlNi	-197^{b} (17.34)
CuZn	-178^{b} (28.66)

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

Table 4-3 The corrosion behavior of three representative copper alloys in 37ºc de-aerated 0.9% NaCl solution.

Alloy	**Eocp** (mV SCE)	**Ez** (mV SCE)	**Ic** (Amps/cm^2)	**Ec** (mV SCE)	**I passivity** (Amps/cm^2)
CuAl	-232	-294	1.61X10^{-2}	7	2.11X10^{-3}
CuAlNi	-186	-231	1.47X10^{-2}	77	3.33X10^{-3}
CuZn	-176	-229	1.33X10^{-2}	37	8.9X10^{-3}

Alloy	**Passive region** (mV SCE)	**Ip** (Amps/cm^2)	**Ep** (mV SCE)	**Corrosion Rate** (mpy)	**Time used to form passive film** (seconds)
CuAl	105 to 294	2.37X10^{-3}	294	2.4X10^{-8}	399
CuAlNi	200 to 430	3.01X10^{-3}	430	8.8X10^{-7}	431
CuZn	No	8.9X10^{-3}	127	9.7X10^{-7}	356

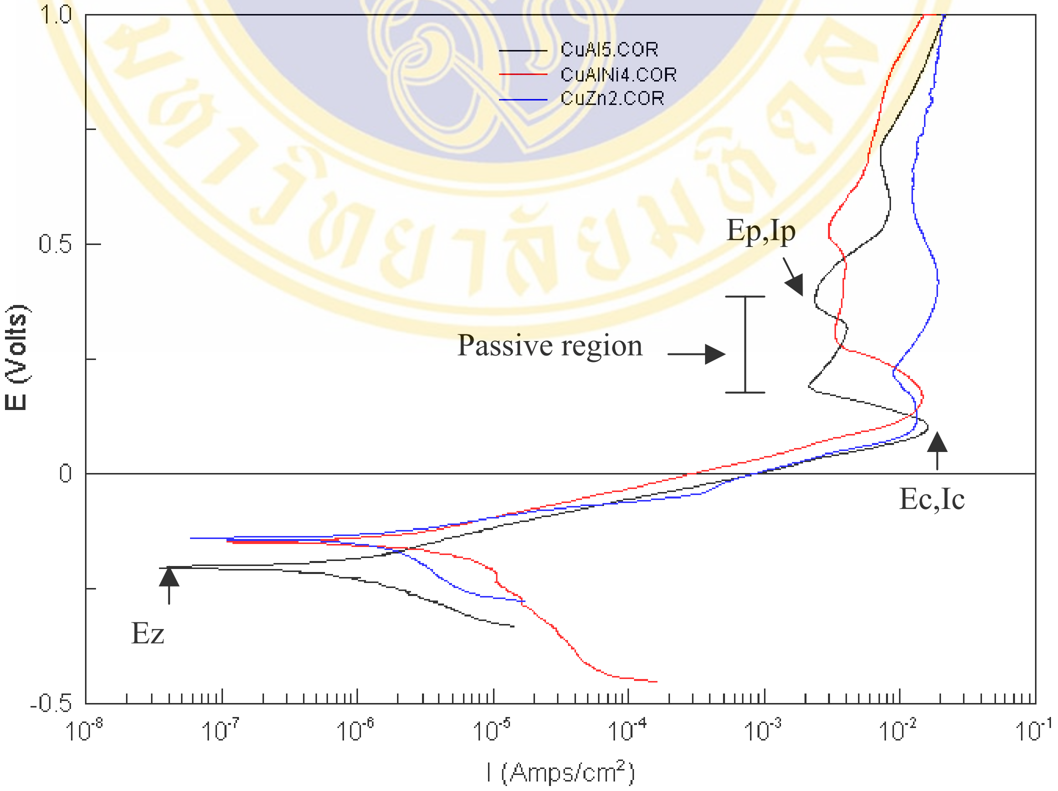

Figure4-1 Potentiodynamic polarization curves for three copper alloys in 37°C de-aerated 0.9% NaCl solution.

From Table 4-2, the mean Eocp of CuAl alloy was lower than that of CuAlNi and CuZn alloy, the value of which was not significantly different. 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, 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. Then the current density of CuAl and CuAlNi were stable in a passive region and then increased again when the curves were up to the breakdown potential.

The curve of CuZn had no passive region because when the potential increased to its breakdown potential (Ep), the current density increased abruptly.

Tables 4-4 to 4-6 shown the comparison of corrosion behavior of these alloys in thermodynamic, kinetics and passivity aspects.

Table 4-4 Thermodynamic of electrocorrosion

Thermodynamic	Eocp	Ez
↑ Noble	CuAlNi , CuZn	CuAlNi , CuZn
Active	CuAl	CuAl

Table 4-5 Kinetics of electrocorrosion

Corrosion rate	
↑ High	CuZn
	CuAlNi
Low	CuAl

Table 4-6 Passivity (Corrosion resistance)

	I passivity	Ep	Passivation Range	Corrosion resistance
↑ High	CuAlNi	CuAlNi	CuAlNi	CuAlNi
	CuAl	CuAl	CuAl	CuAl
Low	CuZn	CuZn		CuZn

SEM pictures of three copper alloys before and after potentiodynamic test in 0.9% NaCl were shown in Figures 4-2 to 4-4. Figure 4-2b and 4-4b showed numerous corrosion products covering the alloy surfaces. Pitting corrosion occurred on the CuAl surfaces. SEM picture of CuZn surface showed crevice corrosion. The CuAlNi surface did not show the presence of any localized corrosion except for the presence of large grains.

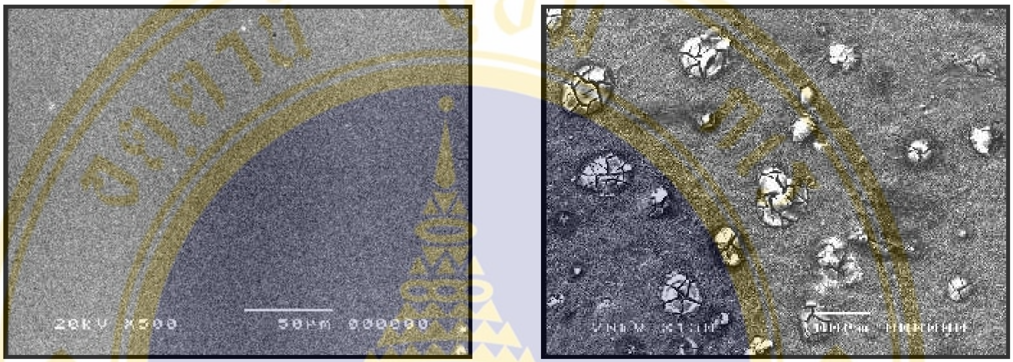

Figure 4-2a Figure 4-2b

SEM pictures of CuAl surface before (a) and after (b) corrosion testing.

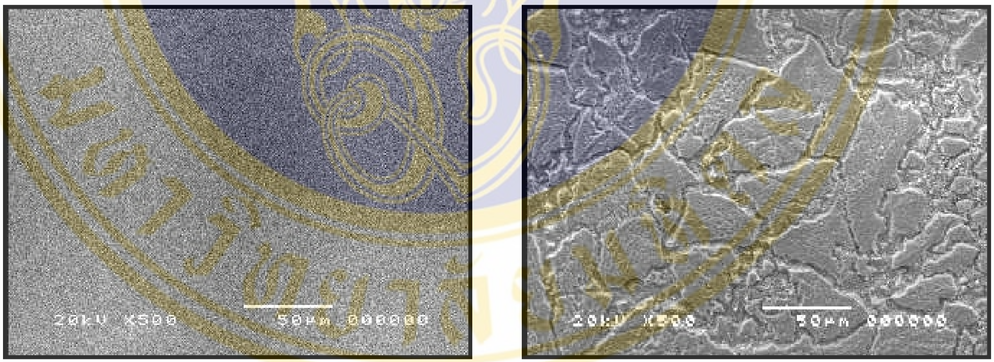

Figure 4-3a Figure 4-3b

SEM pictures of CuAlNi surface before (a) and after (b) corrosion testing

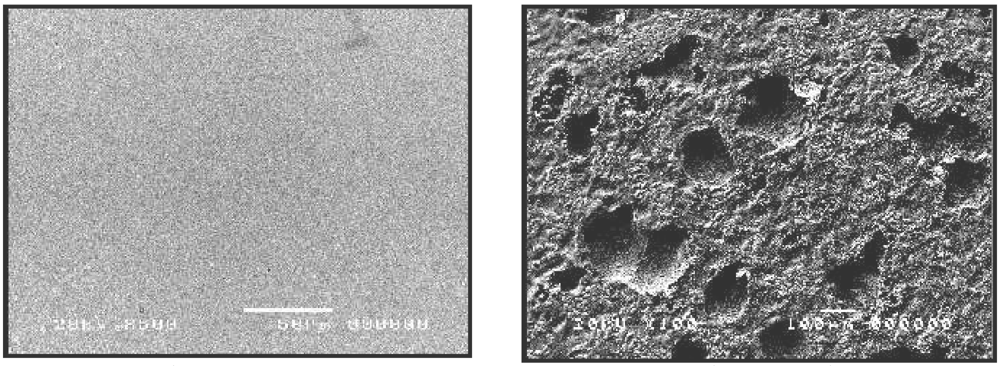

Figure 4-4a Figure 4-4b

SEM pictures of CuZn surface before (a) and after (b) corrosion testing

CHAPTER 5
DISCUSSION

Part I

According to ISO/FDIS 1562: 2003(E) Dentistry-casting gold alloys, the minimum values of 0.2 percent proof stress and percentage elongation after fracture of type III gold alloy are 270 MPa and 5 %, respectively. The percentage elongation after fracture and 0.2 percent proof stress of the three copper alloys in this study were about 50 % and 38.9-92.2 MPa, respectively. The value of 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. It implied that if we used these alloys as post-and-core materials, they will bend, stretch, or otherwise plastically deformed before post fracture. In this aspect, it might be an advantage for removal of post-and-core in some clinical situation. If a post-and-core retained crown subjected to traumatic forces, the post-and-core will bend instead of fracture. It was easier to remove bending post-and-core than fractured post retained in root canal. The 0.2 percent proof stress and ultimate tensile strength implied to the strength of post-and-core materials. Obviously, post-and-core should have high strength for prevention of fracture. ISO/FDIS 1562 did not specify the minimum value of ultimate tensile strength but the ultimate tensile strength of these alloys (206.71-322.91 MPa) was close to that of type I and II gold alloys (23). The alloys used as post and core material should have at least ultimate tensile strength equal to type III gold alloy (421 MPa) (23). 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.

It should be noted that the standard deviation of the mean 0.2 percent proof stress of CuZn was 17.6, which was higher than that of CuAl and CuAlNi. After thoroughly checking, it was unexpectedly shown that 0.2 percent proof stress of one specimen was higher value (69.3 MPa) than that of the others, which ranged from 20.5-45.3 MPa. The external and fractured surface were viewed by microscope and found nothing different from the others. One possibility of the cause might be due to the difficult and different casting procedure of CuZn from the others. However, the detail of microstructure should be identified to clarify the reason of this phenomenon.

Modulus of elasticity could not be presented because there was some error during attachment of the extensometer to the specimens. So, it could not detect strain during the initial stage of applying force. The displacement of the specimens shown on the software was not the real displacement in the initial stage. From our pilot study which determined modulus of elasticity of these copper alloys by using the extensometer attached to the specimen with similar shape, we found the modulus of elasticity to be about 70 GPa, the value of which was lower than that of type III gold alloy (100 GPa) (23). In this aspect, this value is promising to be developed in further study because it was not too low value as that of carbon fiber post, glass fiber post (14-18 GPa)(20,22). If we use these alloys as post-and-core materials, they will not flex like carbon fiber post. Some researcher (21,22) revealed that occlusal loads may cause the carbon fiber post to flex with eventual micromovement of the core, and the cement seal at the margin of the crown may fracture in a short time.

Part II

Potentiodynamic polarization technique is a fundamental and widely used method for corrosion testing in vitro. In the present work, six separated scans were performed for each copper alloy. Some differences between the results of replicated tests may be attributed to small variation in the preparation of replicate specimens, variation of Eocp, lack of pH control and other experimental variables.

From Figure 4-1, the current densities were on the order of 10^{-3} to 10^{-2} A/cm^2, a very high dissolution density, unlike the usual current densities in the passive state, 10^{-8} to 10^{-6} A/cm^2, three to four orders of magnitude lower, for the truly passivating alloys. There was selective dissolution of these alloys. Thus the potential region above Ec shown a complex behavior including selective dissolution of Zn and Al, formation of oxides and chlorides, and the current density limitation resulting from accumulation of corrosion products.

The potentiodynamic curve of CuZn had no passive region. It implied that this alloy has lowest corrosion resistance between these three alloys. While the curve of CuAl had shorter passive region than that of CuAlNi and above Ec, its curve looked like wave because the oxide compounds were oxidized and its protective film changed structure and composition. So, CuAl had lower corrosion resistance than CuAlNi.

The potentiodynamic curve of CuAlNi had 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 (42).

In this study, we did not quantitatively analyze the change of alloy composition in both specimens and electrolyte after corrosion resistance test. So, we could not identify the structures of any dissolved ion, oxides and chlorides compound, passive film, and 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, corrosion products of these alloys also affected their microstructures that might degrade some properties such as mechanical properties.

Additionally, formation of very thin protective film may be due to characters of these alloys and using 0.9% NaCl as test media. Comparing to potentiodynamic curve of copper in 3.5% NaCl (48), they look like in the same pattern (Figure 5-1). The corrosion reaction of copper, especially in a solution containing chloride ions, were 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. Mayer and Nally (49) indicated that 0.9% saline solution was considered to be more aggressive than saliva and its artificial substitutes, because the chloride which was six time higher. Moreover, it lacks of some component which might show a corrosion inhibited action and a buffer capacity such as phosphate. Marek and Topfl (50) 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 condition and the interpretation of in vitro data somewhat hypothetical.

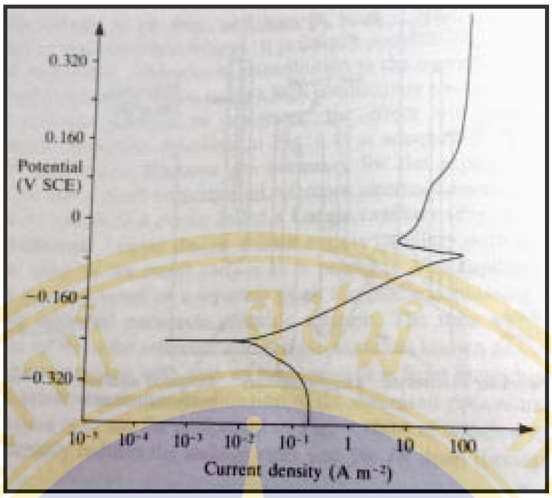

Figure 5-1 Potentiodynamic scan for copper in 3.5% NaCl solution

The potential occurred in the oral cavity has been reported by Ewers and Greener (51), who produced and envelop 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. Regard to the scan conditions in this study, the potential was increased up to 1000mV. The final potential was much higher than the potential occurred in the oral cavity. So, 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 severely corroded alloy surface when 0.9% NaCl was used as test media. Such a high potential and corrosive environment caused the copper alloys corroded aggressively. However, this situation might not have occurred in the oral cavity. Therefore, if someone needs to correlate the corrosion behavior of in vitro study with clinical aspects, he should limit the potential within the potential range of the oral cavity (-58 to +212 mV).

In mechanical property aspect, CuAl seemed to be suitable for post and core material because it had higher 0.2 percent proof stress and ultimate tensile strength than other two alloys, while in corrosion resistance test, CuAlNi had highest corrosion resistance than the others. Thus, both CuAl and CuAlNi showed promising properties for further development as good post-and-core materials.

CHAPTER 6

CONCLUSION

According to this study, the following conclusion could be drawn

1. 0.2 percent proof stress and ultimate tensile strength of CuAl alloy were higher than those of CuAlNi and CuZn alloys.
2. 0.2 percent proof stress of each alloy could not be satisfied ISO 1562: 2003(E) requirements.
3. Corrosion resistance of CuAlNi alloy was higher than that of CuAl and CuZn alloys.
4. The potentiodynamic test method of ISO 10271: 2001 seemed to be not suitable for the study of corrosion behavior of copper alloys under oral condition. So, this study was only the screening test for generalized corrosion of these alloys.
5. CuAl and CuAlNi alloys had a potential for further development as good post-and-core materials.

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BIOGRAPHY

NAME	Miss Usanee Peungpaiboon
DATE OF BIRTH	13 July 1972
PLACE OF BIRTH	Bangkok, Thailand
INSTITUTIONS ATTENDED	Chulalongkorn University, 1996 : Doctor of Dental Surgery Mahidol University, 2004 : Master of Science (Prosthodontics)
POSITION & OFFICE	Department of General Dentistry Faculty of Dentistry, Srinakharinwirot University. 114 Sukhumvit 23, Sukhumvit Rd., Bangkok 10110, Thailand Position : Lecturer Tel. 0-2664-1000 Ext 5090 E-mail: usaneep@swu.ac.th
HOME ADDRESS	133/21 Phetkasem46, Phetkasem Rd., Bangkok 10160, Thailand