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นางสาว เกศรี เชี่ยวชาญลิขกิจ

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

ANALYSIS OF ELEMENTS RELEASED FROM BASE METAL ALLOYS USED IN PROSTHODONTICS



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งานวิจัยนี้มีวัตถุประสงค์ เพื่อวิเคราะห์หาชนิดและปริมาณของธาตุที่ปล่อยออกจากโลหะเหวียงผสมชนิดพื้นฐานในงานทางทันตกรรมประดิษฐ์ ในแบบที่ขัดและไม่ขัดเรียบมันทั้งหมด 8 ชนิด และเพื่อเปรียบเทียบคุณสมบัติการต้านการสึกกร่อนระหว่างโลหะในกลุ่มและระหว่างกลุ่มที่ได้รับการขัดและไม่ขัดเรียบมัน โลหะพื้นฐานทั้ง 8 ชนิดถูกขึ้นรูปและเหวียงเป็นสี่เหลี่ยมลูกบาศก์ที่มีขนาด $3 \times 7 \times 8$ มม. จำนวน 6 ชิ้นในแต่ละกลุ่มตัวอย่าง ชิ้นงานจะถูกทำความสะอาดด้วยเอทานอลและน้ำซึ่งปราศจากไอออน ด้วยเครื่องอัลตราโซนิก จากนั้นแช่ชิ้นงานในหลอดพลาสติก ที่มีสารละลายกรดแลกติก และโซเดียมคลอไรด์ เป็นส่วนประกอบ เก็บไว้ในเตาอบที่อุณหภูมิ 37 องศาเซลเซียส เป็นเวลานาน 336 ชั่วโมง อัตราส่วนพื้นที่ผิวของชิ้นงานโลหะต่อปริมาตรสารละลายคือ $0.60 \text{ ซม}^2/\text{มล}$. เมื่อครบตามเวลาที่กำหนด นำชิ้นงานออกจากหลอดพลาสติก จากนั้นนำสารละลายไปวิเคราะห์หาชนิดและปริมาณของธาตุที่ปล่อยออกมาจากชิ้นงาน ด้วยเครื่องอินดักทีฟ คับเพิล พลาสมา ออฟติกเคิล อิมิชัน สเปกโตรโฟโตมิเตอร์ (ICP-OES) ความเข้มข้นของธาตุที่ได้จากการวิเคราะห์ถูกนำไปใช้ในการวิเคราะห์ทางสถิติ การจำแนกความแปรปรวนแบบหนึ่งปัจจัยที่ระดับความเชื่อมั่น 95% ($\alpha=0.05$)

ผลการทดลองพบว่า กลุ่มชิ้นงานโลหะที่ได้รับการขัดมีการสึกกร่อนและปล่อยธาตุออกมาตั้งแต่ 15.25 ถึง 503.42 ไมโครกรัม/ซม² ส่วนในกลุ่มที่ไม่ได้รับการขัดมีการปล่อยธาตุออกมา ตั้งแต่ 23.22 ถึง 2,426.82 ไมโครกรัม/ซม² ซึ่งปริมาณธาตุที่ปล่อยออกมานั้น ไม่เป็นสัดส่วนกับปริมาณธาตุที่เป็นส่วนประกอบของโลหะตามที่บริษัทผู้ผลิตกำหนด และปริมาณธาตุที่ปล่อยออกจากโลหะทั้งแปดชนิดมีความแตกต่างกันอย่างมีนัยสำคัญทั้งในกลุ่มที่ได้รับการขัดและไม่ได้รับการขัด ($p < 0.001$) และยังพบว่าโลหะผสมที่มีส่วนประกอบของธาตุโครเมียมในปริมาณที่สูง จะมีการต้านการสึกกร่อนได้ดี ธาตุที่ปล่อยออกจากโลหะที่ได้รับการขัดเรียบมันมีปริมาณน้อยกว่าโลหะที่ไม่ได้รับจากขัดเรียบมันอย่างมีนัยสำคัญ ($p < 0.05$) สรุปว่าการขัดเรียบมันที่ผิวของโลหะ สามารถลดปริมาณธาตุที่ปล่อยออกมาจากการสึกกร่อนได้ตั้งแต่ร้อยละ 25-90

ภาควิชา ทันตกรรมประดิษฐ์

สาขาวิชา ทันตกรรมประดิษฐ์

ปีการศึกษา 2548

ลายมือชื่อนิสิต..... น.ศ. เชี่ยวชาญวณิชกิจ

ลายมือชื่ออาจารย์ที่ปรึกษา.....

4676103232 : MAJOR PROSTHODONTICS

KEY WORD: BASE METAL ALLOYS / DENTAL CASTING ALLOYS / ELEMENTS RELEASED / METAL CORROSION / CORROSION RESISTANCE / ICP-OES

KASREE CHIEWCHARNVALIJKIT: ANALYSIS OF ELEMENTS RELEASED FROM BASE METAL ALLOYS USED IN PROSTHODONTICS. THESIS ADVISOR: ASSOC. PROF. ISSARAWAN BOONSIRI, [90] pp. ISBN 974-53-2460-4.

The objective of the research was to analyse the types and amounts of elements released from eight unpolished and polished base metal casting dental alloys used in Prosthodontics. The differences in corrosion resistance among alloys in both unpolished and polished groups were assessed. The differences in the amounts of elements released between unpolished and polished alloys were compared. Eight base metal alloys were cast into a cubic shape measuring 3x7x8 mm. There were six specimens in each group (n=6). Each specimen was ultrasonically cleaned in ethanol and non-ionized distilled water, then immersed in plastic centrifugal tube with lactic acid/NaCl solution and maintained at 37 °C for 336 hours. The ratio of the specimen surface area to volume of solution was 0.60 cm²/ml. Specimens were then removed and the concentration of the elements released in the solution was analyzed using the inductive coupled plasma optical emission spectrophotometer (ICP-OES). The one-way analysis of variance (ANOVA) and the independent sample t-test method were used to analyze with 95% confidence interval ($\alpha=0.05$).

The amount of elements released ranged from 15.25 to 503.42 $\mu\text{g}/\text{cm}^2$ in the polished groups and from 23.22 to 2,426.82 $\mu\text{g}/\text{cm}^2$ in the unpolished groups. The elements released were not proportionate to the bulk alloys' nominal composition. There were statistically significant differences in the total elements released among eight alloys in both unpolished and polished group ($p<0.001$). Alloys composed with a high chromium component were likely to show a higher resistance to corrosion. Polished alloys released significantly less amounts of elements than unpolished alloys ($p<0.05$). In conclusion, the polishing procedure reduces the amount of elements released from 25% up to 90%.

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LIST OF ABBREVIATIONS

ABBREVIATIONS	DESCRIPTION
%	percent
*	Statistically significant difference
®	registered
°C	degree in Celsius
µg/ml	microgram per milliliter
µm	micrometer
Al	Aluminum
ANOVA	analysis of variance
B	Boron
Be	Beryllium
cm	centimeter
cm ²	square centimeter
Co	Cobalt
corp	corporation
Cr	Chromium
et al.	et alii (and others)
etc	et cetera (and so on)
Fe	Iron
fig.	figure

g	gram
hr	hour
ICP-MS	Inductively Coupled Plasma Mass Spectrophotometry
ISO	International Organization for Standardization
Li	Lithium
min.	minute
-ml	milliliter
mm	millimeter
mm ²	square millimeter
Mn	Manganese
Mo	Molybdenum
mol/l	mole per liter
NA	no advice (no information given)
Ni	Nickel
no.	number
SD	standard deviation
Si	Silicon
α	alpha

CHAPTER I

INTRODUCTION

The use of casting dental alloys in dentistry is not a recent concept. In fact, casting dental alloys have been used for many decades as they possess better physical properties than any other materials. The main advantages of using metals in dentistry are their durability, casting ability and rigidity. Previous professional studies have placed emphasis on the physical properties of the metals, whilst others have been more concerned with the biocompatibility in vivo (Schmalz and Garhammer, 2002) and in vitro (Wataha et al, 1998 ; Wataha et al, 2000 ; Al-Hiyasat et al, 2002 ; Craig and Hanks, 1988 ; Sjögren et al, 2000 ; Geis-Gerstorfer et al, 1991).

Base metal alloys are used by dental practitioners around the world as an alternative to gold-based casting alloys. The diversity of alloy composition has been developed to help meet the functional and biological needs of dental patients. However, in spite of the growing use of base metal alloys in dentistry, their biological safety is still in doubt. Critics of base metal alloys suggest that the main disadvantage of using base metal alloys is their corrosion and the release of elements to the adjacent tissue. It is also suggested that the problems of using base metal alloys such as local toxicity (gingival pigmentation, gingivitis), allergy and carcinogenicity result from elements in the alloys being released into the oral tissue during corrosion (Wataha, 2000).

There is now a wide variety of base metal alloys available, which can lead to uncertainty in choosing the optimal alloy for any given situation in each patient.

It is important not only to focus at the physical and mechanical properties, but it is imperative that we also look at the biological safety aspect. We shall also study the alloy's corrosion resistance. Studies have shown that the corrosion resistance of metal alloys is directly correlated to biological compatibility (Blanco-Dalmau, 1982 ; Blanco-Dalmau et al, 1984 ; Jones et al, 1986 ; Lamster et al, 1987 ; Morris, 1987).

In the past, researchers studied the elemental release of the dental casting alloys (Geis-Gerstorfer, 1991 ; Wataha et al, 1991 ; Al-Hiyasat, 2002). The material development is still on going to produce the better material to be used today and in the future. Since the newly developed alloys have changed in their compositions, so as their mechanical and physical properties. The single most relevant property of casting alloy to its biologic safety is its corrosion. It is worthwhile to study about corrosion and the elements released from these base metal alloys which are used in commercial dental laboratories today.

Objectives

1. To find out types and amounts of the element released from eight unpolished and polished base metal casting alloys used in Prosthodontics.
2. To compare the corrosion resistance among different alloys commercially available in both unpolished and polished groups.
3. To compare the corrosion resistance between unpolished and polished alloys.

Research scope

This study aimed to investigate the corrosion properties of base metal alloys used in Prosthodontics. Eight type of alloys used in commercial dental laboratory were selected. Specimens were prepared in the same manner as that of conventional full metal crown and cast post and core in clinical cases. With regards to the corrosion test, the static immersion method was performed. The concentrations of elements released in the corrosive solution were analyzed with Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES).

Agreements

1. For the ease in measuring the surface area, the specimens were designed in cuboid shape but not in dental anatomical form.
2. A Silicone mold was used to form reproducible size of wax patterns.
3. Specimen preparation followed the standard dental laboratory process for full metal crown, casting post and core construction in clinical cases.
4. The ICP-OES was used to identify the elements in the solutions. The ICP-OES is more sensitive than the Atomic Absorption spectroscopy (AAS). The high sensitivity of this machine means that it can effectively detect trace elements from low concentration solutions in parts per billion (ppb). This allowed for the reduction of the specimen' size and solution volume resulting in less material used and provided a saving on costs. The ratio of the specimen surface area to volume of solution was still in the range recommended by the International Organization of Standardization (ISO) for biological studies of medical devices 10993-5 and static immersion test of dental base metal casting alloys ISO 6871-2.

Research limitations

1. This study was performed to measure types and amounts of elements released from base metal alloys into corrosion solution in laboratory conditions (in vitro).
2. The eight base metal alloys used in this study are currently available in three commercial dental laboratories.

Type of research

Experimental research

Proposed benefits

1. To identify types and amounts of the elements released from each base metal casting alloys used in Prosthodontics.
2. To determine whether the corrosion resistances among alloys used in commercial laboratory are different.
3. To determine whether polishing has any effect at reducing an alloys' corrosion.
4. To gain informative data which could be used in future biocompatibility research in dental materials.

Hypotheses

- There is no significant difference in the elements released amongst the eight base metal casting dental alloys ($\alpha=0.05$).
- There is no significant difference in the elements released between unpolished and polished condition in each alloy ($\alpha=0.05$).



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CHAPTER II

LITERATURE REVIEW

Metals and metalloids

A metal is any element that ionizes positively in a solution. During the ionization process, metals release electrons. The existing ability of metal as free positively charged stable ion is the key factor in the behavior of metals and is responsible for many metallic properties that are important in dentistry.

Metalloids, including carbon, silicon, and boron do not always form free positive ions. Their conductive and electronic properties make them ideal components of many alloys.

Physical properties of metals

Properties of metals result from the metallic crystal structure and metallic bonds as below

1. High density due to crystal lattice
2. Electrical and thermal conductivity because of the mobility of valence electrons in crystal lattice
3. Opacity and reflective nature due to the valence electrons absorbing and re-emitting light.
4. Melting points occur when the metallic bonds are overcome by the applied heat. The melting points are higher if the number of valence electrons increases as the metallic bond develops the covalent character. For example, iron (Fe^{3+}) and nickel (Ni^{2+}).

The differences of the distances in the horizontal and vertical directions between metal atoms in a crystal lattice make the differences in properties such as conductivity of electricity and heat, magnetism and strength.

In dentistry, a dental alloy makes up with a collection of randomly oriented crystals each called a "grain". The directional properties are averaged out across the material. Fine-grained structure is desirable to encourage alloys with uniform properties in any direction.

Principles of Metallurgy and Alloys (Craig and Power, 2002)

Metallurgy is the study of metals and alloys. Like liquids, metals can be mixed together. A mixture of metals is called an "alloy". Alloy can be the mixture of two or more different metals. Not all metals will dissolve freely in one another. Phase diagrams are employed to assist understanding of the nature of alloys and metal solubility.

Alloy microstructure

The internal appearance of alloys under light and electron microscopy has been extensively used to describe alloys and interpret alloy behavior. Atomic structure can be determined by x-ray diffraction or high-resolution electron microscopy.

Grains, grain boundaries, and dendrites

Nucleation is the process wherein the first solid alloy particle is formed when the molten alloy cools to the temperature of liquidus. Some alloys have added grain refiner. For example, the fine particles of a high-melting point element such as Ir, will encourage even nucleation throughout the alloy. As the cooling continues, the nuclei grow into crystals, called "grains". The grains enlarge until all liquid is gone and then meet and form the boundaries between one another (at the solidus temperature). At this point, grains can be seen through the light microscope or sometime unaided.

The size of the grains depends on the cooling rate, alloy composition, presence of grain refiners, and other factors. Grain size may influence an alloy's strength, workability, and even susceptibility to corrosion.

Grain boundaries, the junctions where the grains meet, are important because they often contain impurities such as oxides and are the sites of corrosive attack. Grain boundaries can be seen clearly in microscopic view of alloy.

Dendrites result from grains that grow along major axes of the crystal lattice early in freezing process. The dendritic skeleton structure persists to room temperature if the cooling rate of the alloy is too fast to allow equilibrium to occur. The dendritic structure is common in dental alloys and can be seen after etching and polishing the alloy. Dendritic structure indicates that the alloy is not at equilibrium and its presence can increase the corrosion of the alloy.

Cast microstructure

Insoluble impurities in an alloy may be detected at grain boundaries. If gas inclusions are involved, small pits in the bulk of an alloy or at the surface maybe detected. In the body of an alloy, pits may concentrate the stress and contribute to restoration failure. At the surface, pits may enhance corrosion, tarnish, or discoloration from the accumulation of organic debris. Voids in an alloy may result from improper cooling or improper investing.

Properties of alloys

The compositions of dental alloys are dependent on the intended clinical use and environment. For example, a dental crown must have excellent corrosion resistance and must not deform permanently. In each case, alloys composed of elements that optimized the specific properties that are needed most for clinical success are utilized. It is the diversity of possible properties that makes alloys suitable for many clinical dental applications.

Classification of dental casting alloys (Craig and Power, 2002)

Formerly, the American Dental Association (ADA) classified casting alloys into 4 types from type I-IV. The type of alloy depends on its content of gold and platinum group metals. All alloy types were gold-based.

The new classification revised by The Council on Dental Materials, Instruments, and Equipment (1984) is based on noble metal contents of alloys.

1. high-noble with a noble metal content of $\geq 60\%$ wt and a gold content of $\geq 40\%$
2. Noble, with a noble metal content $\geq 25\%$ (no stipulation for gold)
3. Predominately base metal, with a noble metal content $< 25\%$

Base metal alloys offer many advantages such as high strength, stiffness, hardness and notably at a significantly lower cost when compared to noble alloys. Nevertheless, their disadvantages compose with their clinical application. However, from the biologic safety aspect, the main disadvantage of base metal alloys is their low corrosion resistance.

It is commonly find that metal restorations under oral environment, moisture, temperature, acidity and microorganisms are likely to have discoloration, dull or loss of glossy appearance. These are called "tarnish" or some may often say as "corrosion".

Tarnish and Corrosion (Phillips, 1991)

Tarnish and corrosion are difficult to distinguish clinically between corrosion and tarnish and often used as the same meaning. The differentiation between the two was made.

"Tarnish" is a surface discoloration on metal with or a slight loss or alteration of surface luster. In oral cavity, the formation of dental plaque and calculus on the surface of restoration is the main cause of tarnish. The thin film of plaque is composed of microorganisms and mucin. The stain and discoloration are due to bacteria, food debris and drugs containing iron or mercury.

The film deposited and produced tarnish may form or accumulate elements or compounds that chemically attack the metallic surface over time. Often, tarnish is a forerunner of corrosion.

"Corrosion" is an actual deterioration of a metal, caused by the reaction of metal and its environment. Often occurs at metal surface under stress or with intergranular impurities.

Corrosion process involve in oxidation and reduction of metal. Alloys corrode when elements in the alloys ionize (Craig RG, 1997). The initially uncharged elements inside the alloy lose electrons and then become positively charged ions that are then released into the solution. The corrosion properties of metals depend on the ability of atomic centers and electrons to be released in exchange for energy. The amount of energy required depends on the strength of the metallic force and the energy that the released ion can gain by solvating in solution. The facts that metals such as gold or platinum have strong metallic bond, valence electrons are more tightly held, and salvation energies are relatively low. Therefore they are far less likely to corrode.

Corrosion may affect the esthetics, strength and biocompatibility. If corrosion attack occurs extremely localized, it may cause rapid mechanical failure of metal even though the actual loss of material is quite small. This metal disintegration may occur from the result of moisture, atmosphere, acid or alkaline solutions and also some chemicals.

Type of corrosion

There are two general classifications of corrosion reaction (Phillips, 1991).

- I. "Chemical corrosion" or "dry corrosion" is a direct combination of metallic and non-metallic elements. For example, silver discoloration is due to the formation of silversulfide (Ag_2S). There is no need for water or any other fluid electrolytes in this type of corrosion. Chemical corrosion is rarely isolated, it usually coupled with electrochemical corrosion.

II. "Electrochemical corrosion" or "wet corrosion" requires a solution as the pathway for electron transportation. In oral cavity is wet and involved with this type of corrosion. Saliva is a weak electrolyte as it contains salts (Phillips, 1991). The electrochemical properties of saliva depend on its composition, concentration of its components, pH, surface tension and buffering capacity.

Electrolytic corrosion occurs when metal ions pass into solution and hydrogen ions pass out of solution. There are two independent areas, those at which metal dissolves (anodic) and those at which hydrogen ions are discharged (cathodic). Type of electrolytic corrosion are based on the mechanisms that produce these inhomogeneous areas and caused the electric couple action.

1. "Galvanic corrosion" or "dissimilar corrosion", occurs when dissimilar metals touch each other. It is very important, for example, when the surfaces of two different metal restorations are in contact, they produce "electro galvanism" or "galvanic currents". Patients may or may not have symptoms.

2. "Stress corrosion" is commonly found on most dental appliances. It is likely to occur together when there is a fatigue of metal in corrosive environment. For example, repeated removal and insertion of partial denture may build up a severe stress at the grain boundaries. Together with the corrosive environment in oral cavity, the stressed appliance develops "stress corrosion". Irregularities on metal surface such as pits accelerate the corrosion process.

3. "Concentration cell corrosion" or "crevice corrosion" occurs once there are variations in the electrolytes. For example, proximal area where food debris trapped has one type of electrolyte and normal saliva has another at the occlusal area. Therefore, electrolytic corrosion occurs, more likely to attack at the metal surface underneath the layer of food debris. Similarly, the attack produced from where there are differences in oxygen tension between parts of the same restoration, such irregularities of metal surface and pits are in this category.

Alloys corrosion in clinical significance

Adverse reactions of oral mucosa tissue at the adjacent dental alloys were due to direct contact and the accumulated corrosion products from alloys' surface (Wataha, 2000). There were reported of adverse reactions of oral tissues due to dental alloys application such as gingival inflammation, leukoplakia (Moffa, 1982; Eichner, 1983; Hensten-Pettersen, 1992; Morris et al., 1992). Such reactions were claimed to be the result from metal hypersensitivity which initiate by the metal elements released from metal corrosion to the adjacent tissue. Therefore, alloy's biocompatibility is directly correlated with its corrosion property (Blanco-Dalmau, 1982 ; Blanco-Dalmau et al, 1984 ; Jones et al, 1986 ; Lamster et al, 1987 ; Morris, 1987). On the other had, there was report of the increased plaque accumulation might then cause adverse inflammatory reactions in soft tissues adjacent to restorations (Craig and Hanks, 1988).

Alloy's corrosion products may result in local toxicity, allergic reaction, mutagenic or carcinogenicity. Some metal elements have been reported as mutagen or carcinogen such as beryllium and cadmium. However, none has been reported from the use of dental alloys in oral cavity (Wataha, 2000).

Namikoshi et al. (1990) investigated the prevalence of sensitivity to amalgam and casting alloys in 95 randomly selected persons. Six individuals developed positive reactions in epicutaneous patch tests to constituents of cast alloys, such as Cu, Ni, Co, Au, and Zn. In addition, medical devices (pacemakers), jewelry, and dental metallic restorations may cause metal allergy in patients.

Nickel has been shown to be highly allergenic. Therefore, Ni-containing alloys should be avoided in persons with a history of Ni allergy. It is recommended that the uptake of nickel for extremely hypersensitive persons exhibiting nickel allergies should not exceed 0.06 mg/L (Malten and Spruit, 1969). There is a lack of agreement if the application of Palladium (Pd) alloys significantly increases the risk of allergic reactions to this ion. It must be emphasized, however, that many patients (from 34% to 65.5%) who are allergic to nickel are also allergic to Pd (Schaffran et al., 1999). This aspect should

be taken into serious consideration before the use of Pd-containing alloys in patients who are allergic to nickel.

The incidence of nickel hypersensitivity is greater in women 10 times than that in men as they expose to nickel containing jewelry, particularly from pierced earrings. The finding that patients with lack of positive response to nickel-chromium alloy but positive nickel patch tests may relate to passivity of the chromium metal alloyed with nickel as it can greatly reducing the amount of free nickel ions in oral environment (Jones et al, 1986).

It is not yet confirmed of the actual process of biologic interaction of alloys' corrosion products and oral tissue. Moreover, the minimal dosage of metal elements which could cause the adverse reaction is not yet available. Therefore, the use of dental alloys is based on materials' biocompatibility tested in vitro.

Effect of corrosion products to adjacent tissue

It has also been documented that metal ions, which are released from restorations by corrosion, can penetrate dental hard tissues (Söremark et al, 1968)

Corrosion in connection with root fractures of post-retained restorations by several authors (Rud and Omnell, 1970; Silness et al, 1979). It has also been documented that metal ions, which are released from post by corrosion, can penetrate dental hard tissues as corrosion products were observed in dentinal tubules.

Silness et al (1979) proposed the mechanisms of root fracturing due to corrosion. Early stage of corrosion, corrosion products are forced, or migrated into dentin tubules in the post canal walls. The dentinal tubules were filled and blocked with products which can no longer absorb the pressure exerted by the increasing of corrosion products. If the force exceeds the strength of the root, fracturing takes place. The corrosion process continues and the fracture surface is secondarily covered by a layer of corrosion products. The corrosion products may migrate or be forced into periodontal space and show periapical tissue defect.

Kvist et al (1989) indicated that the placement of a post in a root canal did not lower the apical healing or maintenance of periapical health by itself. It was the quality of the root canal filling seal that made the significant. From the technical procedures in placement of a post, the root canal seal might provoke by microbiologic irritants from saliva and cause the defective seal.

Factors affecting alloys' corrosion

1. Alloy's composition

Alloys with high-noble metal content generally release less mass than alloys with little or no noble metal. The elemental release from noble alloys is not proportional to alloy composition but rather influenced by the numbers and types of phases in alloy microstructure and the composition of the phases. In general, multiple-phase alloys release more mass than single-phase alloys.

Some elements are more likely to be released from alloys such as copper, zinc, silver, cadmium and nickel. Elements are less likely to be released from alloys are gold, palladium, platinum and indium. (Wataha et al,1991) ; base-metal alloys (Geis-Gerstorfer et al, 1991)

Alloys containing high chromium (Cr) and molybdenum (Mo) were more likely to have higher corrosion resistance, and so as alloy which has homogeneous surface oxide. They released very low amount of corrosion products (Bumgardner and Lucas, 1995). They play an important role in the formation of the corrosion resistant surface layers.

An increased concentration of chromium and molybdenum in the surface layer lower the dissolution rate of metal in the active phase and provoke the formation of a corrosion resistant film during the passivation procedure. The "self-repair" or the repassivation of the existing pitting and crevice corrosion enhance in corrosion resistance of cobalt-chromium alloys or chromium- riched alloys (Olefjord, 1980, Brune et al, 1984; Brune, 1988)

Geis-Gerstorfer et al (1991) showed that cobalt-based alloys released narrow range of corrosion products. They measured the ion release from casting dental alloys in Ni-Cr-Mo and Co-Cr-Mo. Ni-Cr-Mo alloys slowly released ion in 35 days $0.54\text{-}3,261 \mu\text{g}/\text{cm}^2$. Co-Cr-Mo alloys have narrow range of ion release of $0.43\text{-}34.9 \mu\text{g}/\text{cm}^2$.

2. Conditioning medium : saline, protein-saline, culture medium

Several conditioning solutions were used to accelerate the mass release from casting dental alloys. Nelson et al (1999) suggested that conditioning alloys with saline in combination with 3% bovine-serum-albumin (BSA) solution (Fisher Scientific, Fair Lawn, N.J.) for 168 hours could effectively reduce most alloys' cytotoxicity but not to nickel-chromium alloys. Mass loss during conditioned with this solution were as close to 10-month loss for most alloys.

Conditioning of casting alloys with biologic solutions. The accelerated toxicity testing was suggested to be a useful method to foretell the long-term cytotoxicity by using short term in vitro test. Elemental release was accelerated by removing initial labile elements. But it was noted that all conditioning solutions were not equivalent for the outcome.

Wataha et al (2001) also suggested that high element release during the exposure of alloys to protein conditioning medium corresponded to alloys' low cytotoxicity afterward. In contrary, nickel element release was decreased in the present of BSA.

3. pH of conditioning medium

Dental alloys restorations in oral cavity are obligated to challenge with the intermittent acidity changes all the time. Studies showed that at transient exposure of alloys to acidic oral environment was significantly increase elemental release from nickel-based alloys, but not from high noble or noble alloys (Wataha et al, 1998; Wataha et al, 1999).

There was no change in corrosion resistance of high noble and noble alloys at pH of 4.0. Their element release such as Ag, Cu and Pd was slightly increased at pH

1.0. Unlikely to nickel based alloys which released large amounts of nickel in both pH environments and the release continued to the week after exposure.

4. Conditioning time

Depending on the duration, different elements give out different biological effects due to the uniqueness of interaction of each element with oral tissue. Conditioning time is cooperated with conditioning medium. As it was suggested by Nelson et al (1999) that conditioning the Ni-Cr alloy for 168 hours with either saline or saline/BSA caused more mass release than the unconditioned alloy over 10 months.

Elements released from a specific group of single phase noble and high noble alloys has shown to be higher initially when measured at weekly intervals over a 4-week period (Wataha et al, 1999 ; Geis-Gerstorfer et al, 1991; Al-Hiyasat et al, 2002).

Element released from dental casting alloys into biologic solution is higher in initial state (Messer and Lucas, 1996; Wataha et al, 1992; Wataha and Lockwood, 1998). It also has been shown that initial higher rates of release of elements do not continue over a longer period (Wataha and Lockwood, 1998). In addition, the study of Geis Gerstorfer (1991), the result showed that alloys immersed in medium are likely to corrode rapidly for about 15 days. After this point, the rate of corrosion will decelerate or decrease.

The level of metal ion released increased over the period of the test but was not proportional to bulk alloy composition, especially in relation to Nickel ions and Beryllium ions (Bumgardner and Lucas, 1995).

5. Alloy surface composition

Mülders et al (1996) suggested that there were changes in crystallographic structure of alloys after the corrosion. Also noted that non-precious metal alloys displayed a coarse dendritic structure and an increased in dehomogenization with coarser structure. In contrary, noble alloys had corrosion stable

Alloys' surface compositions were not proportionate to bulk composition. Alloys which had more chromium on the surface had higher corrosion resistance (Wataha and Malcom, 1996)

Polishing procedure caused the changes in alloy's surface composition and therefore it altered the corrosion resistance of the alloy. The "as-cast" condition of an alloy increased elements released from alloy more than the polished condition. Therefore, polished surface alloys are assumed to have better biocompatibility. (Craig and Hanks, 1988).

6. Tooth brushing

No doubt that metal restorations in oral cavity are subjected to mechanical cleaning, "tooth brushing". Study showed that tooth brushing increased element released from dental casting alloys. The effect of brushing alone increased the elemental release of dental casting alloys but in nickel-chrome alloys, the effect continued until the week after. Combination of tooth brushing, acidic solutions and toothpaste could increase nickel element released up to 30-fold in nickel-chrome alloys (Wataha et al, 1999).

7. Cleaning methods

The effect of alloy's cleaning process on the elemental release was determined (Wataha et al, 1992). Cleaning did not change the pattern of elements released but significantly decreased the quantity of elements released. Also, the presence of organic film up to 50 nm thick on alloy's surface was showed after exposure to the medium.

Biocompatibility

From the biocompatibility standpoint, the corrosion of an alloy indicates that some of the elements are available to affect the tissue around it.

It is difficult to predict the biological response even if the elements release from an alloy is known. The reliable way is to measure the biological response directly, either in vitro, in animals, or in humans.

The biocompatibility of noble dental alloys is primarily related to elemental release from these alloys (i.e., their corrosion). Any toxic, allergic or other adverse biological response is primarily influenced by elements released from these alloys into the oral cavity. The biological response is influenced by which elements are released, their concentrations and duration of exposure to oral tissues. For example, short time exposure (1-2 days) of Zinc may not be biologically significant, but the long-term exposure may have significant effects.

In determining the biological response of elemental release from materials in vitro, the release must be measure in the similar condition as it is occurring in clinical situation. Researchers measured the element release at low pH (acidic conditions) for long (30 days) (Geis-Gerstorfer et al, 1991), and short (30 minutes) (Wataha et al, 1998) periods of time to asses the effects from acidic foods and plaque that can produce pH as low as 4 (Aamdal-Scheie et al, 1996).

The differences in alloy's surface affect the biocompatibility of the alloy. Dental crown and bridge casting alloys and nickel-, cobalt-base alloys that have been through the polishing process have good biocompatibility while the unpolished alloys (or as-cast condition) do not have good compatibility (Craig and Hanks, 1988).

The objective of in vitro biocompatibility test is to simulate biological reactions to materials when they are placed on or into tissues of the body. These methods offer less

expensive ways to survey newly developed materials, reducing the probability of surprises when animal usage tests or clinical trials are performed. Without prior laboratory testing of materials, using animals to test materials could become very time-consuming and expensive (Hanks et al, 1996).

Corrosion and cytotoxicity

Corrosion products from nickel-chromium dental alloys decreased cellular proliferation but did not affect cellular morphology or viabilities. Types and amounts of metal ions released, which corresponded to the alloys' reported surface and corrosion properties also correlated to observed decreases in cellular proliferation.

The study of the release of elements from dental casting alloys has been more extensively investigated than cytotoxicologic effects as the elemental release is related to alloy biocompatibility. The elemental release has been reported for high-noble and noble alloys (Wataha et al, 1991; Lappalainen and Yli-Urpo, 1995 ; Johansson et al, 1989), base metal alloys (Johansson et al, 1989 ; Geis Gerstorfer et al,1991) and for other types of alloys and solders (Brune, 1988 ; Vaidyanathan and Prasad, 1981). Most of these studies have focused on measurement of release during the exposure to biologic medium or artificial saliva over periods ranging from 24 hours to 1 month. In most of these studies, initial element release (first 24 hours) is relatively high, followed by a gradual equilibration to a more constant rate over several weeks (Vaidyanathan and Prasad, 1981)

Pure nickel and chromium in particulates, discs, or thin sheets, were used in cell culture. Nickel was found to interfere with various enzyme systems, disrupted intracellular organelles, alter the morphology, decrease cell numbers and increase hemolysis to a significantly greater extent than chromium (Craig and Hanks, 1990).

Evaluation of solid samples of nickel-chromium alloys revealed a very low cytotoxic response of the cultured cells through morphological and ultrastructural

evaluations, viability, synthesis of various proteins, and proliferation (Craig and Hanks, 1988, 1990).

It has been questioned whether short term vitro tests are accurate indicator of alloy biocompatibility in the long term oral condition (Mjör and Hensten-Pettersen, 1983). There are several ways to measure and compare the cytotoxicity of dental casting alloys. In research performed by Sjögren et al (2000), result showed that the agar overlay and the Millipore filter test proved to be less sensitive in regards to the element release testing. Also mentioned, the release of Copper and Zinc is an important factor in the cytotoxic effect.

The changes in cell culture result from the release of metal ion. The monitoring of these changes can describe the biologic response in vitro.

1. Succinic dehydrogenase (SDH) activity
2. Protein production
3. Lactate dehydrogenase (LDH) release

Macrophage cell, fibroblasts and osteoblasts were used in measuring the changes of concentration of the above factors. The concentration of metal ion that could change the metabolism and protein production are usually less than the concentration that could cause cell lysis. Also lower concentration (non-lethal) could cause the cells to secrete protein inflammatory mediators such as cytokines. The secreted cytokine(s) could also be responsible for an inflammation response to such tissues.

Methods for corrosion products measuring

There are several ways to measure corrosion. One way is to measure visually by observing the alloy surface, utilizing electrochemical tests that measure elemental release indirectly through the flow of the released electrons (Fontana MG, 1986).

Atomic Spectroscopy (Skoog et al, 2004)

Atomic spectroscopic methods are used to determine the quality and quantity of elements with their low concentration detection as parts-per-million to parts-per-billion..

In the determination of atomic species by spectroscopy, the sample is volatilized and decomposed into gas-phase atoms and ions. This is the called "atomization", the first and the most critical step in all atomic spectroscopic procedures. The efficiency and reproducibility of the atomization procedure influences the sensitivity, precision and accuracy of the method.

There are several methods to atomize samples for atomic spectroscopic studies. Most widely used atomization methods are inductively coupled plasmas, flames and electrothermal method. Flames and electrothermal atomizers are used in atomic absorption spectrometry, while the inductively coupled plasma is employed in optical emission and in atomic mass spectrometry.

Table 1 Classification of Atomic Spectroscopic Methods (Skoog et al, 2004)

Atomization method	Typical atomization temperature, °C	Types of Spectroscopy	Common name and abbreviation
Inductively coupled plasma	6000-8000	Emission	Inductively coupled plasma atomic emission spectroscopy, ICPAES
		Mass	Inductively coupled plasma mass spectroscopy, ICP-MS
Flame	1700-3150	Absorption	Atomic absorption spectroscopy, AAS
		Emission	Atomic emission spectroscopy, AES
		Fluorescence	Atomic fluorescence spectroscopy, AFS
Electrothermal	1200-3000	Absorption	Electrothermal AAS
		Fluorescence	Electrothermal AFS
Direct-current plasma	5000-10000	Emission	DC plasma spectroscopy, DCP
Electric arc	3000-8000	Emission	Arc-source emission spectroscopy
Electric spark	Varies with time and position	Emission	Spark-source emission spectroscopy
		Mass	Spark-source mass spectroscopy

Only plasma source atomic spectroscopic was reviewed.

Plasma atomizers have been available commercially since the mid-1970s. They have been used for atomic emission, atomic fluorescence and atomic mass spectrometry.

"Plasma" is a conducting gaseous mixture containing a significant concentration of cations and electrons. In argon plasma atomic spectroscopy, radio frequency power source offers the greatest advantage in terms of sensitivity and freedom from interference.

Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

ICP-MS is a multi-element technique for trace element analysis where low detection limits are required (0.0005-1.0 ppb) and for high-precision isotope ratio studies. Sample preparation is more crucial than in ICP-OES, with samples ideally dissolved in 2% HNO₃ v/v, a total dissolved solids content < 0.2 %. If sample solution contains higher concentration of elements, then it must be diluted prior testing.

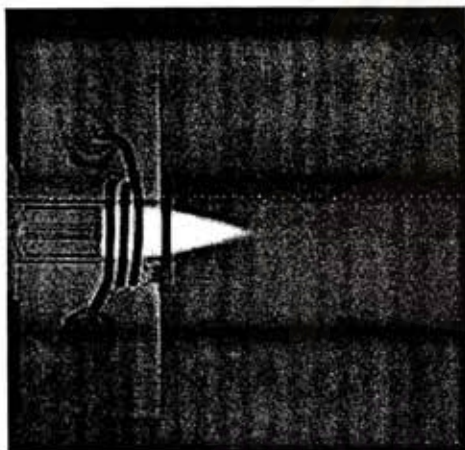
Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

ICP-OES is another multi-element technique for measuring trace metals in liquid solutions. Similar to ICP-MS, the liquid sample is sprayed into argon plasma where the dissolved metals are excited to emit their characteristic ultraviolet and visible radiation. The radiation is dispersed by a grating monochromator and detected with photomultiplier tubes. Radiation wavelength is used to identify the element. The intensity of radiation is used to determine its concentration.

ICP-OES measures elements in the concentration range of 1ppb (part-per-billion) to 1000ppm (parts-per-million) or more. It is a particularly useful technique for measuring samples with high dissolved solids (e.g., slurries and etchants) and samples which contain both high and low concentration elements in the same solution (e.g., waste streams, raw water, RO concentrates, etc).

ICP-OES is a fast multi-element technique with a dynamic linear range and moderate to low detection limits (~0.2-100 ppb). The instrument uses an ICP source to dissociate the sample into its constituent atoms or ions, exciting them to a level where they emit light of a specific characteristic wavelength. Many elements (up to 60 elements) can be screened per single sample run with less than one minute. The samples can be analyzed in a variety of aqueous or organic matrices. There is less chemical interference than flamed AAS, but some spectral interferences are possible and also there are some element detection limitations.

Each analytical technique has its own problems, interferences and advantages. Atomic absorption suffers from severe matrix effects. Therefore, it requires the addition of matrix modifiers and the use of the method of standard additions to increase amount of some elements. ICP-OES suffers from many overlapping spectral interferences from other elements and a very high background emission from the plasma itself, limiting detection limits, while interferences are common in ICP-MS.



Picture 1 Inductively coupled plasma source.

Clinical use of base metal alloys

Nickel sensitivity has been reported by Jones et al (1986) to be in women 10 times more than that in men and 0.8% to 20.7% in men and 9% to 31.9% in women by Blanco-Dalmau et al (1984). The increased percentage of women with nickel sensitivity was due to the chance of contact with nickel-containing jewelry especially pierced earrings (Moffa et al, 1983; Jones et al, 1986). Despite the fact that nickel and chromium are known as allergens, the use of base metal alloys reported to be increased since year 1970 from 30% to 80% of dental restorations (Mjör and Hensten-Pettersen, 1983; Morris, 1987). A few cases have been reported indicating adverse side-effects (Moffa, 1982; Eichner, 1983; Hensten-Pettersen, 1992; Morris et al., 1992).

The American Dental Association (ADA) requires manufactures to put the warning notation on all base metal alloys packages as "CAUTION: As with all nickel-containing alloys, the use of this alloy should be avoided by persons with known nickel sensitivity" (ISO 6871-2).

Morris (1987) showed that 58% of time with routine medical history taking alone had failed in identification screening patient with metal alloys sensitivity. With this unacceptable level of success, additional medical history was recommended to improve screening patients with allergic tendencies and increased exposure to metallic allergens. The improved medical history is as followed (Morris, 1987).

Improved medical history

1. Allergy to medications
2. Allergy to foods
3. Seasonal allergy
4. Dermatologic conditions
5. Problems wearing jewelry
6. Occupation in metal industry
7. History of metallic implant

CHAPTER III

RESEARCH METHODOLOGY

I. Specimens

The following eight types of base metal casting alloys used for fixed prosthesis in commercial dental laboratories were selected for this study. Nominal compositions were provided by the manufacturers (table 1).

1. Commend (Ni-Cr), Alloy Express
2. Commend NB (Ni-Cr), Alloy Express
3. Heraeneum NA (Ni-Cr), Asia Dent
4. Noritake Super Alloy EX-3 (Ni-Cr), NuvoDent : Noritake Dental Supply
5. d-sign 30 (Co-Cr), Dental Vision : Williams
6. 4-All (Ni-Cr), Dental Vision : Williams
7. NNB (Ni-Cr), Dentsply-Sankin : Degussa
8. Discovery (Co-Cr), Alloy Express

Table 2 Alloys' composition in weight percentage (wt%)

Name	Type	Composition % by weight														
		Ni	Co	Cr	Be	Mo	B	Si	Al	Fe	Li	Ga	Nb	C	Mn	Ta
Commend	NiCr	77	-	14	1.8	4.7	-	0.5	2	0.5	-	-	-	0.5	-	-
Commend NB	NiCr	67	-	21	-	8.5	-	-	-	-	-	-	1.75	-	-	1.75
Heraeneum NA	NiCr	59.3	-	24	-	10	-	≤2	-	≤2	-	-	≤2	-	≤2	≤2
Noritake EX-3	NiCr	62.8	-	19.1	-	7.1	-	-	-	-	-	2	-	-	-	-
d-sign 30	CoCr	-	60.2	30.1	-	0.6	0.3	0.9	<1	0.5	<1	3.9	3.2	-	-	-
4-All	NiCr	61.4	-	25.7	-	11	-	1.5	<1	-	-	-	-	<1	-	-
NNB	NiCr	73	-	12	-	10	-	-	NA	-	-	-	-	-	-	-
Discovery	CoCr	-	59.5	31.5	-	5	-	2	-	-	-	-	-	-	-	-

II. Specimen preparation (Sample size: n = 6)



1. Preparation of wax patterns

A silicone mold was used to produce wax patterns in a cuboid shape with dimensions of 3 x 7 x 8 mm. A silicone mold was used to produce wax patterns with reproducible size and shape. Inlay wax (Bego®) was melted and poured into the silicone mold. Once the wax had hardened, the top of the wax was removed with a sharp blade.

2. Preparing the casting ring

Moistened DeguDent® casting ring liner was used to line the casting ring. The base of the liner was checked to make sure it was flush with the top of the casting ring, opposite the sprue base former.

3. Spruing and investing procedure

A sprue was attached to the wax pattern and positioned the wax pattern in place with wax on DeguDent sprue base former, six patterns per each crucible former. The wetting agent [Waxit®, DeguDent (Dentsply)] was sprayed to coat the wax patterns. The excess wetting agent was carefully removed.

The patterns were invested immediately with the rapid heating phosphate-bonded investment material, Deguvest® Impact mixed with Deguvest® liquid. The powder/liquid ratio was 100 g: 20 ml adding 3 ml of distilled water. After premixing the powder and liquid for approximately 30 seconds by hand with a spatula in a clean bowl supplied with Multivac®4 mixing unit by Degussa®, the mixture remained in a vacuum for 30 seconds. Finally, the mixture of investment material was mixed in a vacuum with Multivac®4 for 60 seconds according to the manufacturer's recommendations.

The vacuum-mixed investment material was slowly poured into the casting ring under light vibration. The casting ring was continuously tilted from side to side to avoid air trapping under the patterns. Once the casting ring was filled, the vibrator was immediately turned off. The investment was allowed to sit and harden for 50 minutes (recommended by manufacturer).

4. Wax elimination

The crucible former was removed after the investment material was set. Compressed air was used to remove any loose particles. The burnout was carried out immediately after the investment set. The casting ring was placed in a furnace, preheated to 300°C for 30 minutes. The sprue side was facing down on a ribbed tray to allow the molten wax to flow freely.

5. Preheating and Casting

A temperature of 900°C was maintained for 30 minutes for the final burnout. At this point, the mold was ready for casting.

The crucible for the alloy being cast was placed in the centrifugal casting machine for preheating. Each crucible was used for each type of alloys. The alloy was added to the crucible to be heated in an induction furnace. Meanwhile, the mold was removed from the furnace and visually checked through the sprue to see whether or not it was properly heated and displayed the cherry-red color ideal for casting. The mold was then placed in the cradle of the casting machine. Once the temperature reached 1400°C, the machine was allowed to spin. The molten alloy was centrifugal cast into the casting ring. The ring was removed with casting tongs.

6. Recovery of the casting (Devesting)

After casting, the casting ring was allowed to cool down in room temperature until the red glow has disappeared completely from the button. The casting ring was plunged under running cold water for approximately 15 minutes. The knife and the plaster pliers were used to trim out the investment material. The residual was removed from the casting by using 125- μ m aluminum oxide, Sand blast machine, Heraeus®.

7. Finishing and polishing procedure

The sprues were removed by using the red stone disc. The "Polished" specimen group was finished with a series of finishing and polishing burs (red stone bur, green stone bur and a rubber wheel) as is similar in treating the full metal crown. In order to prevent cross-contamination during polishing, eight set of burs were used for each alloy type. The "Un-polished" specimens were finished and sand-blasted again, but not polished (the process was similar to finishing cast post and core in clinical situations).

Table 3 Label for each specimen

Label	condition	Specimens	Label	condition	Specimens
A1-A6	unpolished	Commend	K1-K6	polished	Commend
B1-B6	unpolished	Commend NB	L1-L6	polished	Commend NB
C1-C6	unpolished	Heraenium NA	M1-M6	polished	Heraenium NA
D1-D6	unpolished	Noritake Super Alloy EX-3	N1-N6	polished	Noritake Super Alloy EX-3
E1-E6	unpolished	d-sign 30	Q1-Q6	polished	d-sign 30
F1-F6	unpolished	4-All	R1-R6	polished	4-All
G1-G6	unpolished	NNB	S1-S6	polished	NNB
H1-H6	unpolished	Discovery	T1-T6	polished	Discovery
-	-	-	Z1-Z6	-	Teflon

8. Specimen measurements

Due to the sensitivity of element testing and possible laboratory processing errors, each specimen was measured again with digital veneer (Mitutoyo, Japan) for its width, length and thickness. Triplicate readings were used to determine the mean for each measurement. Each specimen's surface area was calculated from the mean of each measurement.

9. Cleaning

The specimens were soaked in a detergent solution, Chlorhexidine gluconate 4%w/v (Hibiscrub™, SSL Healthcare) for 5 minutes, scrubbed with a soft bristle brush and then rinsed in running tap water for 5 minutes. The specimens were then rinsed with non-ionized distilled water and ultrasonically cleaned (Transsonic Digital S, Elma ®) in 95% v/v (by volume) ethanol for 5 minutes. The alloys were placed in each container for each type of alloy. At this point, the specimens were removed and ultrasonically cleaned in de-ionized distilled water for 5 minutes. The cleaning procedure was performed to remove any residual particle contaminants from the processing procedures.

III. Preparation of corrosion solution

The corrosion solution used for in vitro testing of the dental alloys is as described in the International Standards Organization (ISO) Standard 10271. This electrolyte was composed of 0.1 mol/L lactic acid and 0.1 mol/L sodium chloride, at a pH of 2.3. The pH level was chosen based on ISO for corrosion tests and studies that have shown that pH can fall to these levels under plaque (Aamdal-Scheie et al, 1996)

Solution preparation

The corrosion solution was prepared as follows:

1. The following was dissolved into the solution and stirred by using magnetic stirrer, Pyro-Magnestir® by LAB LINE.

- 5.85 g of NaCl analytical grade
- 1.0 ml of 90% Lactic acid ($C_3H_6O_3$) analytical grade
- 300 ml of de-ionized distilled water (grade 2) ISO 3696 (1987) was used. It is very low in inorganic, organic or colloidal contaminants. It is also suitable for sensitive analytical purposes, including atomic absorption spectrometry (AAS) and the determination of constituents in trace quantities. It should be produced by multiple distillations, or by deionization or reverse osmosis followed by distillation.

2. The above solution was diluted into 1,000 ml with de-ionized distilled water.

3. The pH was adjusted by using a pH meter (model 420A by Orion). To counter balance the pH, 6 M NaOH and concentrated HCL were used until the solution had reached the target pH of 2.3

IV. Container

Polybutadiene centrifuge tubes (5 ml) were used to immerse specimens. The selected containers were used to avoid adsorption of trace elements on the surface of the container and also to prevent any possible contamination of other elements which could be released from the glass tubes. With the shape of the centrifugal tube, specimens touched the tubes insignificantly. Containers were tightly sealed with tops and parafilm to prevent evaporation.

V. Static immersion test

Each specimen was placed in a polybutadiene centrifugal tube with 3 ml of corrosion solution. The specimen was completely immersed in the solution. The top of the tube was sealed with a para-film M (Pechiney plastic packaging, Menasha) to avoid evaporation of the solution. The approximate surface area of each specimen was 2.0 cm². The ratio of alloy's surface area to solution volume was 0.60 cm²/ml (midrange 0.5-6 cm²/ml), as recommended for biological studies of medical devices by the International Standards Organization (ISO) 10993-5.

VI. Immersion time and condition

The sealed prepared specimens were kept in an oven (Orbital Incubator SI 50, UK) at a constant temperature of 37 °C for 14 days (336 hours).

VII. Control solution

Control solution was used to confirm that there was no metal contaminant in the corrosion solution.

VIII. Negative control

Teflon pieces were prepared with the same size and shape as the alloy specimens. Teflon was used as a negative control material, according to the ISO standard 10993-5. Each Teflon piece was immersed in corrosion solution for the same period of time as the specimens.

IX. Chemical Analysis

An Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) was Spectro Ciros^{CCD}, Spectro Analysis Instruments Germany. Sample solutions were diluted by a factor of 100 (sample ID. A-Z) with 2% high-purity nitric acid (sub-boiling distillation system, Seaster Chemicals, USA). ICP-OES was used to identify the types and amounts of elements in the solution. Triplicate absorbance readings per element were made for each sample. Each reading was used to determine the mean concentration of the different elements in parts per million (ppm) released from the alloys.

Table 4 ICP-OES : Instrumental parameters

Radiofrequency (RF) Power	1300 watts
Coolant gas flow rate	12.0 L/min
Auxillary gas flow rate	1.0 L/min
Nebulizer gas flow rate	1.0 L/min

Table 5 Metal elements we looked for and their wavelengths used in ICP-OES reading

Element	Wavelengths (nm)
Molybdenum (Mo)	202.030
Boron (B)	249.773
Beryllium (Be)	313.042
Manganese (Mn)	257.611
Silicon (Si)	251.612
Lithium (Li)	670.780
Nickel (Ni)	341.476
Iron (Fe)	239.562
Cobalt (Co)	230.786
Chromium (Cr)	284.325
Aluminum (Al)	167.078

The outcome from ICP-OES was calculated with its software and gave out the concentration of each element in sample solution (ppm). There were 3 ml of solution in each sample. The concentration of element in sample solution in ppm ($\mu\text{g}/\text{ml}$) was used to calculate the actual amount of element in sample. The element released from each alloy would be report in microgram per square centimeter of surface area of alloy (as recommended for the outcome report of static immersion test in $\mu\text{g}/\text{cm}^2$ by ISO 6871-1, 6871-2)

Amount of element in solution (μg) = concentrations ($\mu\text{g}/\text{ml}$) x solution volume (ml)

Amount of element released per alloy's surface area ($\mu\text{g}/\text{cm}^2$)
 = amount of element in solution (μg) / alloy's surface area (cm^2)

The amounts of element released per alloy's surface area ($\mu\text{g}/\text{cm}^2$) were used in statistical analysis.

X. Statistical analysis

The SPSS for Windows 11.5 version program (SPSS Inc., Chicago) was used to analyze and calculate the followings:

1. Descriptive analysis for means and standard deviation of each group of specimens.
2. One-Sample Kolmogorov-Smirnov was carried out to assess the normal distribution of the data.
3. One-Way Analysis of Variance (ANOVA) was performed to assess the differences among the means of total elements released in eight alloys.
4. Tamhane's T2 test was used to identify the possible differences among means of the elements released from the alloys when there was a significant difference from One-way ANOVA.
5. An Independent sample t-test was used to test and verify the mean differences of elements released between unpolished and polished group in each alloy.

The data was analyzed with 95% confidence interval ($\alpha=0.05$).



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CHAPTER IV

RESULTS

Descriptive statistics

- Part I Means and standard deviations of total elements released from unpolished and polished alloys.

Inferential statistics

- Part II Comparison of mean total elements released among eight alloys in unpolished condition
- Part III Comparison of mean total elements released among eight alloys in polished condition
- Part IV Comparison of mean total elements released from each alloy between unpolished and polished conditions

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Descriptive Statistics

Part I. Means and standard deviations of element released from base metal casting dental alloys.

Eight base metal alloys were used in this study. Six nickel-based alloys were Commend, Commend NB, Heraenium NA, Noritake Super Alloy EX-3, 4-All and NNB. Two cobalt-based alloys were Discovery and d-sign 30. The alloys were prepared into unpolished and polished condition with sample sized of six in each group (n=6). Alloys' nominal composition determined the anticipated elements released from alloys' specimens which were nickel (Ni), cobalt (Co), chromium (Cr), beryllium (Be), molybdenum (Mo), boron (B), aluminum (Al), silicon (Si), iron (Fe), lithium (Li), manganese (Mn).

Mean elements released from unpolished and polished alloys were shown in table 6. Some elements such as molybdenum, boron and lithium were under method detection limit (see raw data in appendix A).

Table 6 Mean elements released from unpolished and polished alloys ($\mu\text{g}/\text{cm}^2$)

GROUP	TYPE	NI	CO	CR	BE	MO	B	AL	SI	FE	LI	MN	TOTAL
Commend	NiCr	509.71	-	40.27	73.85	-	-	980.89	18.28	-	-	-	1623.01
Commend NB	NiCr	8.81	-	-	-	-	-	-	16.32	-	-	-	25.13
Heraenium NA	NiCr	11.85	-	-	-	-	-	-	18.12	71.76	-	33.87	135.59
Noritake EX-3	NiCr	181.31	-	66.22	-	-	-	-	-	3.87	-	-	251.40
d-sign 30	CoCr	-	49.44	24.05	-	-	-	-	-	-	-	-	73.48
4-All	NiCr	2.25	-	-	-	-	-	270.06	18.19	-	-	-	290.50
NNB	NiCr	739.64	-	104.83	-	-	-	1478.46	99.26	4.62	-	-	2426.82
Discovery	CoCr	-	4.75	-	-	-	-	-	18.47	-	-	-	23.22
Commend (P)	NiCr	402.52	-	50.74	50.16	-	-	-	-	-	-	-	503.42
Commend NB (P)	NiCr	1.79	-	-	-	-	-	-	16.67	-	-	-	18.46
Heraenium NA (P)	NiCr	1.08	-	-	-	-	-	-	15.56	-	-	-	16.65
Noritake EX-3 (P)	NiCr	44.43	-	19.54	-	-	-	-	29.62	0.80	-	-	94.39
d-sign 30 (P)	CoCr	-	2.42	-	-	-	-	-	14.55	-	-	-	16.98
4-All (P)	NiCr	1.45	-	-	-	-	-	-	14.06	-	-	-	15.51
NNB (P)	NiCr	429.50	-	67.79	-	-	-	-	-	3.27	-	-	500.55
Discovery (P)	CoCr	-	1.04	-	-	-	-	-	14.21	-	-	-	15.25
Teffon		-	-	-	-	-	-	-	-	-	-	-	-

(-) : data not available due to method detection limit; (P) : polished condition

Means and standard deviations of total elements released from unpolished condition were shown in table 7 and figure1. In unpolished condition, NNB had the highest amount of element released ($2426.82 \mu\text{g}/\text{cm}^2$) while Discovery had the lowest amount of element released ($23.22 \mu\text{g}/\text{cm}^2$).

Table 7 Total elements released ($\mu\text{g}/\text{cm}^2$) from unpolished alloys after 336 hours of immersion in 0.1 mol/L Lactic acid/ 0.1 mol/L Sodium Chloride, pH=2.3

Alloy	Type	Mean	SD	Min.	Max.
Discovery	CoCr	23.22	3.61	18.05	28.19
Commend NB	NiCr	25.13	5.45	18.05	33.42
d-sign 30	CoCr	73.48	9.97	65.31	92.35
Heraenium NA	NiCr	135.59	17.39	113.62	156.93
Noritake EX-3	NiCr	251.40	49.22	189.35	318.43
4-All	NiCr	290.50	32.51	253.58	338.92
Commend	NiCr	1623.01	87.92	1475.55	1735.08
NNB	NiCr	2426.82	176.66	2238.56	2666.80

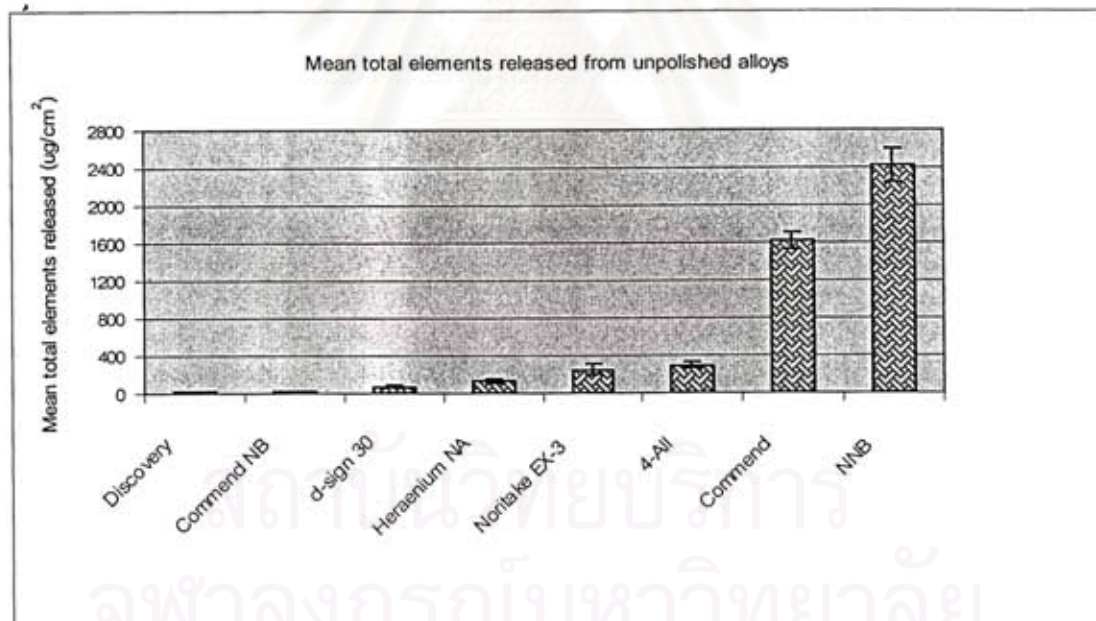


Figure 1 Total elements released from unpolished alloys after 336 hours of immersion in 0.1 mol/L Lactic acid/ 0.1 mol/L Sodium Chloride, pH=2.3

Means and standard deviations of total elements released from eight alloys in polished condition were shown in table 8 and figure 2. Discovery had the lowest amount of elements released ($15.25 \mu\text{g}/\text{cm}^2$) while Commend had the highest elements released ($503.42 \mu\text{g}/\text{cm}^2$).

Table 8 Mean total elements released from polished alloys in $\mu\text{g}/\text{cm}^2$ after 336 hours of immersion in 0.1 mol/L Lactic acid/ 0.1 mol/L Sodium Chloride, pH=2.3

Alloy	Type	Mean	SD	Min.	Max.
Discovery (P)	CoCr	15.25	1.08	13.83	17.06
4-All (P)	NiCr	15.51	1.25	13.49	16.96
Heraenium NA (P)	NiCr	16.65	3.52	13.00	22.73
d-sign 30 (P)	CoCr	16.98	2.51	14.12	20.45
Commend NB (P)	NiCr	18.46	3.92	14.01	24.16
Noritake EX-3 (P)	NiCr	94.39	12.64	76.23	111.62
NNB (P)	NiCr	500.55	26.54	475.85	550.26
Commend (P)	NiCr	503.42	37.68	433.33	530.62

(P) indicated the polished condition of alloy

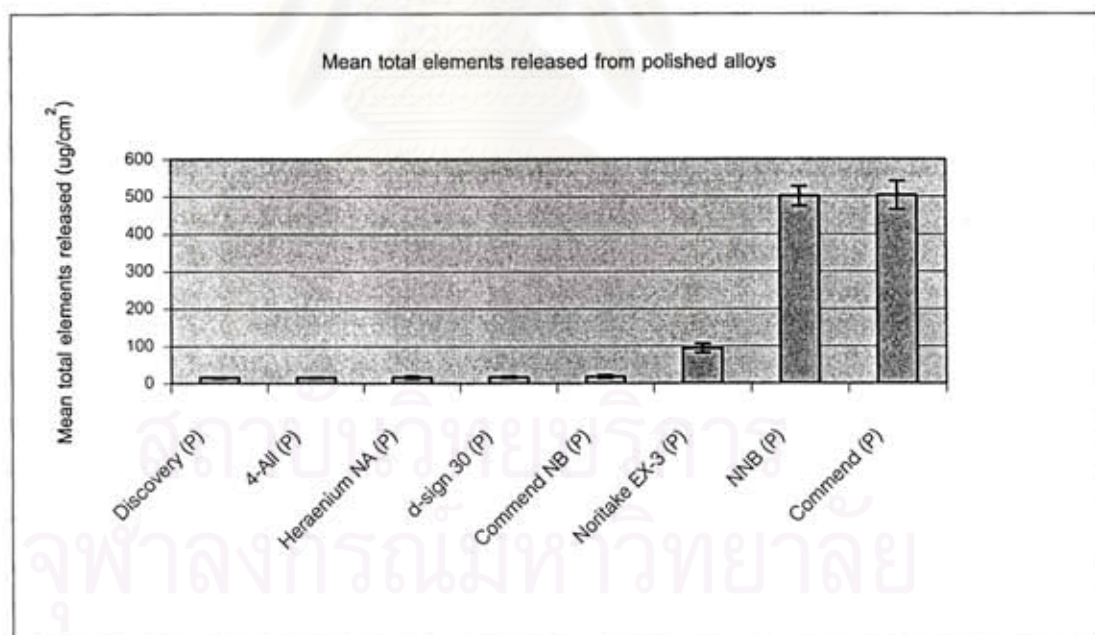


Figure 2 Total elements released from polished alloys in $\mu\text{g}/\text{cm}^2$ after 336 hours of immersion in 0.1 mol/L Lactic acid/ 0.1 mol/L Sodium Chloride, pH=2.3

Means and standard deviations of total elements released from each alloy were compared between unpolished and polished conditions in table 9 and figure 3. Polished alloys released less amounts of elements than the unpolished alloys.

Table 9 Comparisons of mean total elements released between unpolished and polished alloys ($\mu\text{g}/\text{cm}^2$)

ALLOY	Unpolished alloy		Polished alloy	
	Mean	SD	Mean	SD
Discovery	23.22	3.61	15.25	1.08
Commend NB	25.13	5.45	18.46	3.92
d-sign 30	73.48	9.97	16.98	2.51
Heraenium NA	135.59	17.39	16.65	3.52
Noritake EX-3	251.40	49.22	94.39	12.64
4-All	290.50	32.51	15.51	1.25
Commend	1623.01	87.92	503.42	37.68
NNB	2426.82	176.66	500.55	26.54

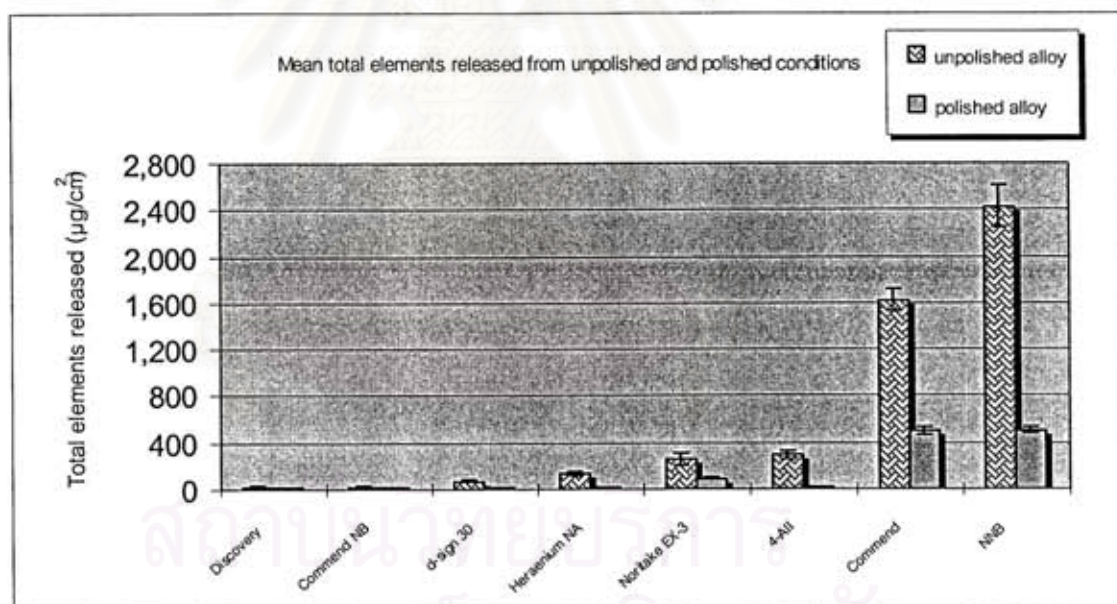


Figure 3 Mean total elements released from unpolished and polished alloys in $\mu\text{g}/\text{cm}^2$ after 336 hours of immersion in 0.1 mol/L Lactic acid/ 0.1 mol/L Sodium Chloride, pH=2.3

The amount of elements released between the polished and unpolished alloys were markedly different. To compare the differences of mean total elements released in percentage, the formula showed below was used in the calculation. The recession percentage of elements released from unpolished alloys to the polished one was showed in table 10.

$$\text{Recession percentage} = \frac{\text{mean}_{\text{unpolished}} - \text{mean}_{\text{polished}}}{\text{mean}_{\text{unpolished}}} \times 100$$

Table 10 Recession percentage of total elements released from eight base metal alloys

Alloy	mean		Recession percentage
	unpolished	polished	
Discovery	23.22	15.25	34.31
Commend NB	25.13	18.46	26.55
d-sign 30	73.48	16.98	76.90
Heraenium NA	135.59	16.65	87.72
Noritake EX-3	251.40	94.39	62.45
4-All	290.50	15.51	94.66
Commend	1623.01	503.42	68.98
NNB	2426.82	500.55	79.37

Comparison of elements released to bulk metal composition

In comparing elements released to bulk metal composition, the total elements released and alloys' composition were used to calculate as the following formula.

$$\text{proposed element release} = \frac{\text{percentage of nickel composition} \times \text{total elements released}}{100}$$

The amounts of element released were not proportionate to bulk metal composition (see appendix C). For example, Commend composed of 77% nickel and had mean total elements released of 1,623.01 $\mu\text{g}/\text{cm}^2$. Despite the proposed nickel element released of 1,249.72 $\mu\text{g}/\text{cm}^2$, Commend had actual nickel element released of 509.71 $\mu\text{g}/\text{cm}^2$.

$$\begin{aligned} \text{proposed ni-element release} &= \frac{77 \times 1623.01}{100} \mu\text{g}/\text{cm}^2 \\ &= 1249.72 \mu\text{g}/\text{cm}^2 \end{aligned}$$

Inferential Statistics

The data were tested for normal distribution by using the Kolmogorov-Smirnov test at 95% confidence interval ($\alpha = 0.05$) (Index B). Parametric statistics, One-way ANOVA, Tamhane test, One-sample independent t-test were used for data analysis in this study. Tamhane test was used because equal variances were not assumed in the data.

Part II. Comparison of mean total elements released among eight alloys in unpolished condition

Eight base metal alloys used in Prosthodontics were used in the study. Base metal alloys in solution are likely to corrode once the electrochemical circuit is completed. Metal elements are then released into the environment such as adjacent tooth structure and/or gingival tissue. Since the main compositions of alloys are similar, alloys are assumed to have similar corrosion properties.

Ho : Alloys released the same amount of elements in unpolished condition ($\alpha = 0.05$)

Ha : At least one pair of alloys is different in mean total elements released ($\alpha = 0.05$)

One-way ANOVA test showed that at least one pair of means is different ($p < 0.001$). In the assumption of ANOVA test, variances of group means are homogenous. Despite the variances of group means were not homogenous but the Welch and Brown-Forsythe test confirmed the significant statistics of the outcome from ANOVA test.

Test of Homogeneity of Variances

TOTAL

Levene Statistic	df1	df2	Sig.
15.086	7	40	.000

ANOVA

TOTAL

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	3.5E+07	7	4934475.219	920.975	.000
Within Groups	214315.4	40	5357.884		
Total	3.5E+07	47			

Robust Tests of Equality of Means

TOTAL

	Statistic ^a	df1	df2	Sig.
Welch	449.156	7	16.267	.000
Brown-Forsythe	920.975	7	8.825	.000

a. Asymptotically F distributed.

Most of the alloys were significantly different in means of total elements released among unpolished alloys. The amounts of elements released in some alloys were not significantly different (Commend NB and Discovery, Noritake Super Alloy EX-3 and 4-All) (see table11).

Discovery and Commend NB had the lowest amount of total elements released. Discovery was significantly different from Noritake Super Alloy EX-3 ($p < 0.05$) and highly significantly different from d-sign30, Heraenium NA, 4-All, Commend and NNB ($p < 0.001$). Commend NB showed a significant difference from Noritake Super Alloy EX-3 and highly significantly different from d-sign30, Heraenium NA, 4-All, Commend and NNB ($p < 0.001$). 4-All, Commend and NNB were highly significantly different from one another and were highly significantly different from other alloys ($p < 0.001$).

The sequences of alloys were arranged by the amount of elements released from the lowest to the highest as follow: Discovery and Commend NB, d-sign 30, Heraenium NA, 4-All and Noritake Super Alloy EX-3, Commend, NNB.

Table 11 Multiple comparisons showed statistically significant differences in mean total elements released from unpolished alloys.

BRAND mean \pm SD	Discovery 23.22 \pm 3.61	Comm.NB 25.13 \pm 5.45	d-sign 30 73.48 \pm 9.97	Herae.NA 135.59 \pm 17.39	Noritake 251.40 \pm 49.22	4-All 290.50 \pm 32.	Commend 1,623.01 \pm 87.92	NNB 2,426.82 \pm 176.
Discovery								
Commend NB								
d-sign 30	**	**						
Heraenium NA	**	**	*					
Noritake EX-3	*	*	*	*				
4-All	**	**	**	**	**			
Commend	**	**	**	**	**	**	**	
NNB	**	**	**	**	**	**	**	**

*p<0.05

**p<0.001

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Part III. Comparison of mean total elements released among eight alloys in polished condition

The alloy specimens were polished in the same manner as that done in clinical cases of polishing full metal crowns. Due to the polishing process, the surfaces of the alloys were shiny and glossy. Since the main compositions of alloys are similar (as they are base metal alloys) they are assumed to have the same amount of corrosion product.

Ho : Alloys released the same amount of elements in polished condition ($\alpha = 0.05$)

Ha : At least one pair of alloys is different in mean total elements released ($\alpha = 0.05$)

One-way ANOVA test showed that at least one pair of means is different ($p < 0.001$). In the assumption of ANOVA test, variances of group means are homogenous. Despite the variances of group means were not homogenous but the Welch and Brown-Forsythe test confirmed the significant statistics of the outcome from ANOVA test.

Test of Homogeneity of Variances

TOTAL

Levene Statistic	df1	df2	Sig.
6.281	7	40	.000

ANOVA

TOTAL

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	2039206	7	291315.152	1004.310	.000
Within Groups	11602.59	40	290.065		
Total	2050809	47			

Robust Tests of Equality of Means

TOTAL

	Statistic ^a	df1	df2	Sig.
Welch	372.552	7	16.507	.000
Brown-Forsythe	1004.310	7	10.609	.000

a. Asymptotically F distributed.

Multiple comparisons showed that Discovery, 4-All, Heraenium NA, d-sign 30 and Commend NB were not statistically significantly different from one another ($p>0.05$). They released the lowest amount of mean total elements. They were highly significantly different from NNB and Commend ($p<0.001$).

Means of elements released from Discovery and 4-All were significantly different from Noritake Super Alloy EX-3 ($p<0.05$). Heraenium NA, d-sign 30 and Commend NB were highly significantly different from Noritake Super Alloy EX-3 ($p<0.001$).

Means of NNB and Commend were not statistically significantly different from each other. Both of them were highly significantly different from other Alloys.

Discovery, 4-All, Heraenium NA, d-sign 30 and Commend NB had less amount of elements released than Noritake Super Alloy EX-3, NNB and Commend (table 12)

Table 12 Multiple comparisons showed statistically significantly differences in mean total elements released from polished alloys

BRAND	Discovery	4-All	Herae.NA	d-sign30	Comm.NB	Noritake	NNB	Commend
Discovery								
4-All								
Heraenium NA								
d-sign 30								
Commend NB								
Noritake EX-3	*	*	**	**	**			
NNB	**	**	**	**	**	**	**	
Commend	**	**	**	**	**	**	**	**

* $p<0.05$

** $p<0.001$

Part IV. Comparison of mean total elements released from each alloy between unpolished and polished conditions

Both unpolished and polished specimens of each alloy are composed of the same metals. To simulate post and core alloy for endodontic treated tooth, unpolished specimens were prepared by the same process as in clinical cases. After the alloys were cast, they were left to cool and then cleaned by sand blasting with aluminum oxide.

The polished specimens were meant to imitate the full metal crown alloy. They were finished and polished to glossy shine. Despite the difference in surface treatment, both unpolished and polished specimens share the same composition. Therefore, it was assumed that they would release the same amount of metal elements.

Mean total elements released from unpolished and polished specimens of each alloy were compared by using One-sample independent t-test at 95% confidence interval ($\alpha=0.05$).

Ho : There is no statistically significant difference in mean total elements released between unpolished and polished alloys ($\alpha = 0.05$)

Ha: Mean total elements released from unpolished and polished alloys were statistically significantly different from each other ($\alpha = 0.05$)

There were statistically significant differences between unpolished and polished group in each alloys ($p<0.05$) (table 13).

1. There was a statistically significant difference between means total elements released of unpolished and polished Commend ($p<0.001$)
2. There was a statistically significant difference between means total elements released of unpolished and polished Commend NB ($p=0.035$)

3. There was a statistically significant difference between means total elements released of unpolished and polished Heraenium NA ($p < 0.001$)
4. There was a statistically significant difference between means total elements released of unpolished and polished Noritake Alloy EX-3 ($p < 0.001$)
5. There was a statistically significant difference between means total elements released of unpolished and polished d-sign 30 ($p < 0.001$)
6. There was a statistically significant difference between means total elements released of unpolished and polished 4-All ($p < 0.001$)
7. There was a statistically significant difference between means total elements released of unpolished and polished NNB ($p < 0.001$)
8. There was a statistically significant difference between means total elements released of unpolished and polished Discovery ($p < 0.001$)

Table 13 Independent t-test comparing between unpolished and polished conditions of each alloy

Independent samples t-test between unpolished and polished group in each alloy

ALLOYS	Levene's Test			t-test for Equality of Means						
		F	Sig.	t	df	Sig. (2-tailed)	Mean Differ difference	Std.Error difference	95% Confidence Interval	
									Lower	Upper
Commend	a	2.35	0.156	28.67	10.00	0.000	1119.59	39.05	1032.58	1206.60
	b			28.67	6.78	0.000	1119.59	39.05	1026.63	1212.55
Commend NB	a	0.47	0.509	2.43	10.00	0.035	6.67	2.74	0.57	12.78
	b			2.43	9.09	0.037	6.67	2.74	0.48	12.86
Heraenium NA	a	9.47	0.012	16.42	10.00	0.000	118.94	7.24	102.80	135.08
	b			16.42	5.41	0.000	118.94	7.24	100.74	137.14
Noritake EX-3	a	9.18	0.013	7.57	10.00	0.000	157.01	20.74	110.79	203.23
	b			7.57	5.66	0.000	157.01	20.74	105.49	208.53
d-sign 30	a	4.02	0.073	13.46	10.00	0.000	56.51	4.20	47.16	65.86
	b			13.46	5.63	0.000	56.51	4.20	46.07	66.95
4-All	a	9.82	0.011	20.70	10.00	0.000	274.99	13.28	245.39	304.58
	b			20.70	5.01	0.000	274.99	13.28	240.87	309.10
NNB	a	23.65	0.001	26.41	10.00	0.000	1926.27	72.93	1763.77	2088.77
	b			26.41	5.23	0.000	1926.27	72.93	1741.20	2111.34
Discovery	a	4.82	0.053	5.18	10.00	0.000	7.97	1.54	4.54	11.39
	b			5.18	5.88	0.002	7.97	1.54	4.19	11.75

a. Equal variances assumed

b. Equal variances not assumed

CHAPTER V

DISCUSSION

Base metal casting alloys are used extensively in dental profession especially in economical concern cases. One of the crucial requirements of any metal or alloy to be used in oral cavity is that it must not produce corrosion products that could be harmful to the body. The main disadvantage of base metal alloys is their corrosion which relates to their biological compatibility (Blanco-Dalmau, 1982 ; Blanco-Dalmau et al, 1984 ; Jones et al, 1986 ; Lamster et al, 1987 ; Morris, 1987).

Despite the fact that these corrosion products might not be easily recognized when the corrosion process is not marked, there were reports of allergy, hypersensitivity and other effects from dental alloys in patients (Jones et al, 1986). It has been demonstrated that elements released from alloy's corrosion could cause intra-oral reactions (such as redness, swelling and pain of the oral mucosa and lips) (Hensten-Pettersen, 1992). The incidence of reported side-effects from dental materials in prosthodontics was about 1:400 (Hensten-Pettersen and Jacobsen, 1991).

In spite of the similarity of alloys' nominal compositions, the amounts of elements released from eight base metal alloys were significantly different. Minor differences in alloys' components may affect the surface characteristics of the alloys. Moreover, it was reported that the types and amount of elements released from the casting alloy related to their surface composition but not to the bulk composition (Wataha and Malcom, 1996).

In unpolished condition, Discovery which is cobalt-based alloy had the lowest amount of total elements released ($23.22 \mu\text{g}/\text{cm}^2$) while NNB, nickel-based alloy, had the highest ($2,426.82 \mu\text{g}/\text{cm}^2$). Interestingly, in polished condition, five out of eight alloys (Discovery, 4-All, Heraenium NA, d-sign 30 and Commend NB) had comparable amounts of total elements released. They also had the lowest amounts of elements released. Commend and NNB released the highest amount of total elements. They had nearly an equal amount of elements released.

With regards to nickel-based alloys in unpolished condition, Commend NB has the lowest amount of total elements released ($25.13 \mu\text{g}/\text{cm}^2$) whilst NNB had the highest amount of total elements released ($2,426.82 \mu\text{g}/\text{cm}^2$). In polished condition, 4-All, Heraenium NA and Commend NB were not significantly different in amounts of total elements released. They released the lowest amounts of elements. NNB and Commend had the highest amount of total elements released. The amounts of total elements released were relatively similar.

As for the biological compatibility aspect, it is prudent for dentists to choose an alloy which has good corrosion resistance or in other words, an alloy which releases the lowest amounts of elements. Discovery had the best corrosion resistance for cobalt-based alloys. Amongst nickel-based alloys, Commend NB had the best corrosion resistance. Once the alloys were polished, Discovery, 4-All, Heraenium NA, d-sign 30 and Commend NB have no noticeable differences in corrosion property.

However, the amount of element released from 4-All greatly changed after being polished. 4-All had the best corrosion resistance. It is worth noting that 4-All had the most amount of chromium (25.7%) as a composition comparing to the other nickel-based alloys. Similar notion to Discovery (31.5%) and d-sign 30 (30.1%), both alloys had large amounts of chromium in their composition and had less amount of elements released.

The result of Cobalt-chromium alloys and alloys with high chromium concentration showed higher corrosion resistance because chromium corrosion product may form the passivation layer film as explained in the previous study (Olefjord, 1980, Brune et al, 1984; Brune, 1988)

The high amounts of total element released from Commend and NNB coincide with the fact that they were composed of chromium as low as 14% and 12% respectively.

The polishing process removed the irregularities and impurities of the casting process from the surface of alloy specimens. As a result, the polished alloy specimens had smoother surfaces which gave less contact area with the solution and also

decrease the chances of having crevice corrosion at the pits and irregular surfaces. In the body of an alloy, pits may concentrate the stress and contribute to restoration failure. At the surface, pits may enhance corrosion, tarnish, or discoloration from the accumulation of organic debris.

The surface composition of the polished and unpolished alloy specimen may be different as stated by Wataha (1992) that the surface compositions of the alloys were not the same as that in bulk composition until the 12.5 nm-dept mark was reached. If the surface of the alloy composed of high amount of chromium, it will have higher corrosion resistance (Olefjord, 1980, Brune et al, 1984; Brune, 1988).

This study showed that polished alloys significantly released lower amount of elements than unpolished alloys ($p < 0.05$). In particular, the polishing procedure decreased the amount of elements released by approximately 25 percent and as high as 90 percent. Our result concurs with the study of Craig and Hanks (1988) stating that most alloys were less biocompatible in the "as-cast" condition than in the polished condition.

The elements released from the alloy were not proportionate to alloy's bulk composition because the casting process may affect the surface composition and characteristics of the alloys. These findings mirrored the results of previous studies (Messer, 2000; Wataha et al, 1992). For example, an alloy composed of 77% nickel (Commend) only released a nickel element of 31.40% from total elements released. Commend had 14% of chromium in composition but there were only 2.48% of chromium elements in the amount of total elements released (appendix C). This result confirmed that the nominal composition given by the manufacturers only may not be used as the indication of choosing optimal alloys for the patients.

Moreover, the value of critical elements such as nickel element is worth looking for since nickel is well-known to cause allergy. 4-All released the lowest amount of elements released after polished (table 6).

Discovery had better corrosion resistance than d-sign 30 as Discovery had fewer amount of cobalt element and total elements released than d-sign 30 in both unpolished and polished condition (table 6).

Comparing the elements released in this study to those in the other studies

The data concurred with the study by Geis-Gerstorfer (1991), showing nickel-Chromium alloys had a wide range of elements released with the values of 25.13-2426.82 $\mu\text{g}/\text{cm}^2$ whilst the values of element released from Cobalt-Chromium alloys were not as wide (23.22-73.48 $\mu\text{g}/\text{cm}^2$) in unpolished condition. In polished condition Nickel-Chromium alloys had value of 15.51-503.42 $\mu\text{g}/\text{cm}^2$, while Cobalt-Chromium alloys had a narrower range (15.25-16.98 $\mu\text{g}/\text{cm}^2$).

The amount of elements released from both Nickel-based and Cobalt-based alloys dramatically decreased in polished condition. Polished alloys had less corrosion and released fewer amount of elements.

Alloys in polished condition had better corrosion resistance than those in unpolished conditions. This finding supported the study by Craigs and Hanks (1988) stating that alloys that have been through the polishing process possess better biocompatibility in comparison to those in unpolished condition.

To simulate the post and core, the unpolished alloy specimens were prepared in the same manner as that done in preparation the dental posts. Alloys were cast and cleaned but not polished. The elements released from alloys in such condition were far greater than the polished one. This may take into the account of that reported by Silness et al (1979), anticipating that root fracture might be caused by the corrosion of dental posts. The corrosion products found in the dentinal tubules and on the fractured surface were analyzed as metal elements combined with demineralized dentin products. So as documented that metal ions, which are released from restorations by corrosion, can penetrate dental hard tissues (Söremark et al, 1968)

Alloys' corrosion resistance also depends on their composition. In this study, it was clear that alloys which had less elements released composed of high amount of chromium in their component. It supports many studies which stated that alloys containing high chromium (Cr) and molybdenum (Mo) were more likely to have higher corrosion resistance as they released very low amount of corrosion products. Chromium and Molybdenum play an important role in the formation of the corrosion resistant surface layers. (Bumgardner and Lucas, 1995; Olefjord, 1980; Brune et al, 1984; Brune, 1988)

Implications of the results of this study

Nominal composition and physical properties of dental casting alloys given by manufacturers may not give enough information when faced with the decision of choosing the optimal alloy. This study also showed that there was a wide range of the corrosion resistance amongst the alloys, despite their similar composition. It is crucial for dental personnel to gain enough medical history from patient, to inform patient for the possible allergic responses prior to the use of base metal alloys. Additional medical history was recommended to improve screening patients with allergic tendencies and increased exposure to metallic allergens (Morris, 1987).

The polishing procedure could greatly reduce the corrosion products from dental casting alloys. The casting post and core are likely to corrode and are prone to producing more corrosion products than full metal crown. It is essential to finish and polish dental casting alloys prior to insertion of prostheses in patients.

For economical reasons, base metal alloys are still in use in the dental industry. It is therefore essential that dentists are fully aware of the data with regards to alloys and the consequences of using them. Therefore there is a need for more research to help understand better the effects of metal elements on oral tissue and to discover alternative options to increase an alloy's corrosion resistance.

Methodology of this study

Eight base metal casting alloys used in this study are currently used commercially in dental laboratories for the production of fixed prostheses, particularly for full metal crown and casting post and core. Specimen preparations were prepared as recommended by the manufacturers. Individual sets of dental burs were used for each alloy to prevent any cross contamination between alloys. The polishing procedure in this study was identical to that done in dental laboratories and in dental practices to simulate the actual process of prostheses production in clinical cases.

Instrumentation of this study

The specimens' dimensions were measured with a digital vernier (Mitutoyo, Japan) by one examiner. Triplicate readings for each measurement determined the mean of each specimen' dimension which was then used to calculate the surface area in square centimeters. Although stereomicroscope with Image Pro Plus (ML9300 Meiji, Japan) was used to measure and calculate the surface area of the specimens for trial, it was impossible to obtain any precise dimension. Due to the glossy and shiny surface of the polished specimens, the reflected light interfered with the reading of the specimens' margins. Therefore, it was not selected for specimens' measurement.

It would be more accurate to measure the surface area that has irregularities by using the Profilometer (Talyscan 150 and Talymap England) including the 3D program. Unfortunately the 3D program is not yet commercially available. This instrument is used in surface roughness measurement. With the 3D program, each line reading from surface roughness would be gathered and formed into the three dimensional map. The actual surface area would then be illustrated and calculated into square micrometers. The fine detail process of measurement could consume an incredible amount of time. Each square millimeter of surface would take at least fifteen minutes to read or 25 hours per square centimeter.

Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) was used to analyze metal elements in sample solutions. This machine is used in multiple element

analysis. It is capable of reading different types and amounts of metal elements at the same time. The sensitivity of ICP-OES is superior to the Atomic Absorption Spectrophotometer which needs a specific type of lamp to read a specific type of metal element.

In order to avoid background interference for iron and zinc elements, and to avoid error from excessive dilutions, ICP-MS was not selected. Inductively Coupled Plasma Mass Spectrophotometer has higher sensitivity but if the concentration of the metal elements was too high, it would need to be a more diluted solution. Although, the amount of some trace element such as Molybdenum (Mo) was too low to measure and as a result it would be preferable to use ICP-MS for such particular element. However, the key elements (nickel, cobalt, chromium, etc) were suitable with ICP-OES.

Limitation of the study

This body of work was performed to investigate corrosion properties of casting dental alloys in vitro. The solution used in static immersion test was recommended from the International Organization of Standardization (ISO) 6871-1, 2 to gain the information of the type and amount of metal ions released from dental base metal casting alloys.

The findings from this study showed the type and amount of metal ion released from eight base metal casting alloys. Also, it proved scientifically that the polishing procedure increases the alloy's corrosion resistance. This study is not able to offer data and findings of the effect of corrosion product to oral mucosal tissue.

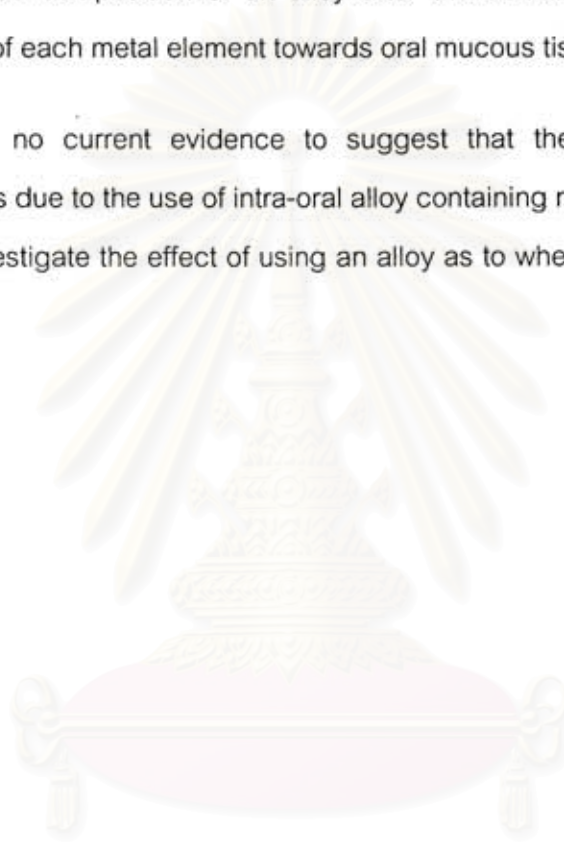
Recommendations for future study

The surface contact area is important factor in biocompatibility of dental alloy usage. Surface composition of an alloy is not proportionate to the alloy's bulk composition. It is the surface composition that plays the important role in an alloy's corrosion behavior and production of the elements released.

It is vital to study an alloy's surface structure and surface composition to understand more about alloy's properties. As suggested, the properties of casting alloy depend basically on its structure. The different composition of alloys could therefore affect the changes in the crystallographic structure of alloys (Mülders et al, 1996).

Future study should place the emphasis on alloy's corrosion process, the change of surface composition of an alloy after the corrosion process and specific tissue reactions of each metal element towards oral mucous tissue.

There is no current evidence to suggest that the direct cause of nickel hypersensitivity is due to the use of intra-oral alloy containing nickel. Yet, long term study is needed to investigate the effect of using an alloy as to whether it could induce nickel sensitivity.



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CHAPTER VI

CONCLUSION

There are currently a wide range of dental casting alloys commercially available. Once the decision has been made to opt for a base metal alloy as an alternative to gold based alloys, it is important to consider the alloy's properties especially in regards to its corrosion resistance.

Elements released were not proportionate to an alloy's nominal composition. So consideration of nominal composition is not sufficient in determining an alloy's corrosion property. Alloys composed with a high chromium component were likely to show a higher resistance to corrosion.

It is the responsibility of each and every dentist to know the identity, the constituent and the possible subsequent side effects of an alloy being used in restoration. A patient's history of allergic reactions and hypersensitivity are the most important factors to consider.

The polishing procedure may lessen the risk of side effects from alloys. The study points to the fact that the polishing procedure significantly reduces the amount of metal elements released by-removing the irregularities from alloys' surface.

This study was unable to conclusively prove which alloy was the best to use in clinical situations but it encourages dental practitioners to be more concerned with regards to dental casting alloys and their corrosion properties. Yet, the complete biologic effect of dental alloys is not currently available and the result of the nickel usage is still ambiguous. The use of dental materials requires informed and full consideration of the risk-benefit ratio.

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APPENDIX A

Surface area of alloy specimens and their elements released ($\mu\text{g}/\text{cm}^2$)

Alloy	No.	area	Concentration of Analyte in Sample ($\mu\text{g}/\text{cm}^2$)											total
			Ni	Co	Cr	Be	Mo	B	Al	Si	Fe	Li	Mn	
Commend	A1	1.85	494.20	ND	40.75	68.16	ND	ND	955.84	19.26	ND	ND	ND	1578.20
	A2	1.90	556.50	ND	41.61	81.23	ND	ND	1037.51	18.24	ND	ND	ND	1735.08
	A3	1.86	504.54	ND	42.00	77.98	ND	ND	994.53	19.99	ND	ND	ND	1639.04
	A4	1.88	526.61	ND	38.72	77.21	ND	ND	991.88	17.19	ND	ND	ND	1651.61
	A5	1.87	468.89	ND	35.22	68.36	ND	ND	885.57	17.52	ND	ND	ND	1475.55
	A6	1.85	507.53	ND	43.33	70.20	ND	ND	1020.03	17.47	ND	ND	ND	1658.55
Commend NB	B1	1.83	14.14	ND	ND	ND	ND	ND	ND	19.27	ND	ND	ND	33.42
	B2	1.89	6.53	ND	ND	ND	ND	ND	ND	11.52	ND	ND	ND	18.05
	B3	1.88	6.11	ND	ND	ND	ND	ND	ND	16.02	ND	ND	ND	22.12
	B4	1.82	9.63	ND	ND	ND	ND	ND	ND	13.62	ND	ND	ND	23.25
	B5	1.86	9.79	ND	ND	ND	ND	ND	ND	19.45	ND	ND	ND	29.24
	B6	1.88	6.66	ND	ND	ND	ND	ND	ND	18.02	ND	ND	ND	24.68
Heraenium NA	C1	1.90	9.83	ND	ND	ND	ND	ND	ND	12.28	50.15	ND	52.37	124.64
	C2	1.91	11.08	ND	ND	ND	ND	ND	ND	12.97	75.22	ND	35.47	134.74
	C3	1.89	14.88	ND	ND	ND	ND	ND	ND	18.96	95.75	ND	27.33	156.93
	C4	1.82	12.91	ND	ND	ND	ND	ND	ND	20.44	56.94	ND	37.80	128.09
	C5	1.85	11.36	ND	ND	ND	ND	ND	ND	22.27	96.24	ND	25.64	155.51
	C6	1.88	11.02	ND	ND	ND	ND	ND	ND	21.77	56.22	ND	24.60	113.62
Noritake EX-3	D1	1.88	147.50	ND	53.45	ND	ND	ND	ND	ND	3.10	ND	ND	204.04
	D2	1.86	228.08	ND	85.55	ND	ND	ND	ND	ND	4.80	ND	ND	318.43
	D3	1.85	138.44	ND	47.98	ND	ND	ND	ND	ND	2.93	ND	ND	189.35
	D4	1.85	174.14	ND	63.86	ND	ND	ND	ND	ND	4.03	ND	ND	242.03
	D5	1.82	195.77	ND	70.35	ND	ND	ND	ND	ND	4.14	ND	ND	270.26
	D6	1.84	203.92	ND	76.15	ND	ND	ND	ND	ND	4.21	ND	ND	284.29
d-sign 30	E1	1.90	ND	54.70	21.45	ND	ND	ND	ND	ND	ND	ND	ND	76.15
	E2	1.88	ND	65.83	26.52	ND	ND	ND	ND	ND	ND	ND	ND	92.35
	E3	1.93	ND	44.44	22.75	ND	ND	ND	ND	ND	ND	ND	ND	67.18
	E4	1.84	ND	45.01	23.79	ND	ND	ND	ND	ND	ND	ND	ND	68.80
	E5	1.94	ND	44.44	20.86	ND	ND	ND	ND	ND	ND	ND	ND	65.31
	E6	1.84	ND	42.19	28.92	ND	ND	ND	ND	ND	ND	ND	ND	71.11
4-All	F1	1.87	2.22	ND	ND	ND	ND	ND	278.23	15.79	ND	ND	ND	296.24
	F2	1.84	4.06	ND	ND	ND	ND	ND	277.21	22.49	ND	ND	ND	303.75
	F3	1.81	1.29	ND	ND	ND	ND	ND	235.33	16.96	ND	ND	ND	253.58
	F4	1.79	0.89	ND	ND	ND	ND	ND	236.11	16.99	ND	ND	ND	253.99
	F5	1.84	1.78	ND	ND	ND	ND	ND	318.87	18.27	ND	ND	ND	338.92
	F6	1.85	3.27	ND	ND	ND	ND	ND	274.59	18.65	ND	ND	ND	296.51
NNB	G1	1.92	661.50	ND	94.43	ND	ND	ND	1387.47	90.81	4.34	ND	ND	2238.56
	G2	1.90	721.79	ND	102.37	ND	ND	ND	1406.24	99.08	4.25	ND	ND	2333.73
	G3	1.92	672.36	ND	94.19	ND	ND	ND	1394.95	91.68	4.13	ND	ND	2257.31
	G4	1.87	820.54	ND	116.49	ND	ND	ND	1616.36	108.36	5.05	ND	ND	2666.80
	G5	1.90	793.60	ND	112.81	ND	ND	ND	1557.22	104.51	5.21	ND	ND	2573.35
	G6	1.92	768.07	ND	108.71	ND	ND	ND	1508.53	101.15	4.74	ND	ND	2491.19

Note 1. ND.= Not detectable due to method detection limit

Alloy	Concentration of Analyte in Sample (ug/cm ²)													
	No.	area	Ni	Co	Cr	Be	Mo	B	Al	Si	Fe	Li	Mn	total
Discovery	H1	1.88	ND	3.41	ND	ND	ND	ND	ND	20.71	ND	ND	ND	24.11
	H2	1.88	ND	8.62	ND	ND	ND	ND	ND	16.70	ND	ND	ND	25.32
	H3	1.88	ND	2.60	ND	ND	ND	ND	ND	20.72	ND	ND	ND	23.32
	H4	1.91	ND	4.08	ND	ND	ND	ND	ND	16.24	ND	ND	ND	20.32
	H5	1.85	ND	2.45	ND	ND	ND	ND	ND	15.60	ND	ND	ND	18.05
	H6	1.88	ND	7.34	ND	ND	ND	ND	ND	20.86	ND	ND	ND	28.19
Commend (P)	K1	1.77	411.40	ND	53.92	49.09	ND	ND	ND	ND	ND	ND	ND	514.41
	K2	1.83	346.17	ND	43.36	43.80	ND	ND	ND	ND	ND	ND	ND	433.33
	K3	1.79	421.80	ND	46.26	59.02	ND	ND	ND	ND	ND	ND	ND	527.08
	K4	1.79	420.26	ND	54.93	51.48	ND	ND	ND	ND	ND	ND	ND	526.67
	K5	1.84	424.27	ND	47.76	58.59	ND	ND	ND	ND	ND	ND	ND	530.62
	K6	1.81	391.24	ND	58.22	38.95	ND	ND	ND	ND	ND	ND	ND	488.41
Commend NB (P)	L1	1.82	1.59	ND	ND	ND	ND	ND	ND	12.42	ND	ND	ND	14.01
	L2	1.82	1.59	ND	ND	ND	ND	ND	ND	22.57	ND	ND	ND	24.16
	L3	1.82	1.74	ND	ND	ND	ND	ND	ND	16.94	ND	ND	ND	18.69
	L4	1.83	1.09	ND	ND	ND	ND	ND	ND	15.24	ND	ND	ND	16.32
	L5	1.84	2.04	ND	ND	ND	ND	ND	ND	13.58	ND	ND	ND	15.63
	L6	1.84	2.67	ND	ND	ND	ND	ND	ND	19.25	ND	ND	ND	21.92
Heraenium NA (P)	M1	1.82	0.85	ND	ND	ND	ND	ND	ND	12.15	ND	ND	ND	13.00
	M2	1.72	2.31	ND	ND	ND	ND	ND	ND	14.36	ND	ND	ND	16.67
	M3	1.79	0.54	ND	ND	ND	ND	ND	ND	22.19	ND	ND	ND	22.73
	M4	1.81	1.44	ND	ND	ND	ND	ND	ND	14.32	ND	ND	ND	15.76
	M5	1.78	0.54	ND	ND	ND	ND	ND	ND	13.13	ND	ND	ND	13.68
	M6	1.84	0.80	ND	ND	ND	ND	ND	ND	17.23	ND	ND	ND	18.04
Noritake EX-3 (P)	N1	1.88	39.35	ND	9.81	ND	ND	ND	ND	26.85	0.22	ND	ND	76.23
	N2	1.87	49.31	ND	23.77	ND	ND	ND	ND	38.32	0.22	ND	ND	111.62
	N3	1.85	41.66	ND	18.27	ND	ND	ND	ND	29.40	0.61	ND	ND	89.94
	N4	1.81	43.24	ND	18.59	ND	ND	ND	ND	26.42	0.84	ND	ND	89.08
	N5	1.85	41.57	ND	18.87	ND	ND	ND	ND	31.93	1.58	ND	ND	93.95
	N6	1.85	51.46	ND	27.93	ND	ND	ND	ND	24.81	1.31	ND	ND	105.50
d-sign 30 (P)	Q1	1.85	ND	1.77	ND	ND	ND	ND	ND	12.84	ND	ND	ND	14.61
	Q2	1.81	ND	1.10	ND	ND	ND	ND	ND	13.01	ND	ND	ND	14.12
	Q3	1.83	ND	4.33	ND	ND	ND	ND	ND	14.66	ND	ND	ND	18.98
	Q4	1.82	ND	2.46	ND	ND	ND	ND	ND	15.30	ND	ND	ND	17.75
	Q5	1.80	ND	3.14	ND	ND	ND	ND	ND	17.31	ND	ND	ND	20.45
	Q6	1.82	ND	1.75	ND	ND	ND	ND	ND	14.19	ND	ND	ND	15.94
4-AlI (P)	R1	1.78	1.53	ND	ND	ND	ND	ND	ND	14.92	ND	ND	ND	16.45
	R2	1.76	1.55	ND	ND	ND	ND	ND	ND	11.94	ND	ND	ND	13.49
	R3	1.79	0.81	ND	ND	ND	ND	ND	ND	14.91	ND	ND	ND	15.72
	R4	1.79	1.12	ND	ND	ND	ND	ND	ND	15.84	ND	ND	ND	16.96
	R5	1.78	1.54	ND	ND	ND	ND	ND	ND	13.19	ND	ND	ND	14.72
	R6	1.75	2.17	ND	ND	ND	ND	ND	ND	13.56	ND	ND	ND	15.73

Note 1. ND.= Not detectable due to method detection limit.

Alloy	Concentration of Analyte in Sample (ug/cm ²)													
	No.	area	Ni	Co	Cr	Be	Mo	B	Al	Si	Fe	Li	Mn	total
NNB (P)	S1	1.84	437.05	ND	66.56	ND	ND	ND	ND	ND	3.88	ND	ND	507.50
	S2	1.82	408.23	ND	64.34	ND	ND	ND	ND	ND	3.28	ND	ND	475.85
	S3	1.82	417.00	ND	64.77	ND	ND	ND	ND	ND	3.58	ND	ND	485.36
	S4	1.78	423.26	ND	70.03	ND	ND	ND	ND	ND	2.10	ND	ND	495.38
	S5	1.84	419.35	ND	66.37	ND	ND	ND	ND	ND	3.24	ND	ND	488.97
	S6	1.83	472.08	ND	74.66	ND	ND	ND	ND	ND	3.52	ND	ND	550.26
Discovery (P)	T1	1.77	ND	1.46	ND	ND	ND	ND	ND	13.75	ND	ND	ND	15.21
	T2	1.74	ND	0.55	ND	ND	ND	ND	ND	13.28	ND	ND	ND	13.83
	T3	1.80	ND	1.20	ND	ND	ND	ND	ND	14.10	ND	ND	ND	15.30
	T4	1.78	ND	0.98	ND	ND	ND	ND	ND	16.08	ND	ND	ND	17.06
	T5	1.76	ND	0.62	ND	ND	ND	ND	ND	13.99	ND	ND	ND	14.61
	T6	1.82	ND	1.43	ND	ND	ND	ND	ND	14.08	ND	ND	ND	15.51
Teflon	Z1	1.78	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Z2	1.78	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Z3	1.78	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Z4	1.78	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Z5	1.78	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Z6	1.78	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Note 1. ND.= Not detectable due to method detection limit

(Method detection limits (MDLs) calculate from ten times the standard deviation of reagent blank solution, (n=10)

multiplied by the overall dilution factor of 140 (w/w))

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Appendix B

One-sample Kolmogorov-Smirnov test for normal distribution

One-Sample Kolmogorov-Smirnov Test

GROUP		NI	CO	CR	BE	MO	B	AL	SI	FE	LI	MN	TOTAL
Commend	Kolmo-Smirnov	0.48	-	0.57	0.59	-	-	0.60	0.61	-	-	-	0.59
	Sig. (2-tailed)	0.98	-	0.90	0.87	-	-	0.86	0.85	-	-	-	0.88
Commend NB	Kolmo-Smirnov	0.63	-	-	-	-	-	-	0.49	-	-	-	0.49
	Sig. (2-tailed)	0.82	-	-	-	-	-	-	0.97	-	-	-	0.97
Heraenium NA	Kolmo-Smirnov	0.67	-	-	-	-	-	-	0.59	0.65	-	0.57	0.51
	Sig. (2-tailed)	0.76	-	-	-	-	-	-	0.87	0.80	-	0.90	0.96
Noritake EX-3	Kolmo-Smirnov	0.42	-	0.37	-	-	-	-	-	0.63	-	-	0.41
	Sig. (2-tailed)	1.00	-	1.00	-	-	-	-	-	0.82	-	-	1.00
d-sign 30	Kolmo-Smirnov	-	0.86	0.49	-	-	-	-	-	-	-	-	0.64
	Sig. (2-tailed)	-	0.45	0.97	-	-	-	-	-	-	-	-	0.81
4-All	Kolmo-Smirnov	0.43	-	-	-	-	-	0.56	0.63	-	-	-	0.58
	Sig. (2-tailed)	0.99	-	-	-	-	-	0.91	0.83	-	-	-	0.89
NNB	Kolmo-Smirnov	0.45	-	0.49	-	-	-	0.67	0.48	0.58	-	-	0.49
	Sig. (2-tailed)	0.99	-	0.97	-	-	-	0.76	0.98	0.89	-	-	0.97
Discovery	Kolmo-Smirnov	-	0.66	-	-	-	-	-	0.76	-	-	-	0.43
	Sig. (2-tailed)	-	0.78	-	-	-	-	-	0.61	-	-	-	0.99
Commend (P)	Kolmo-Smirnov	0.69	0.56	0.51	0.46	-	-	-	-	-	-	-	0.69
	Sig. (2-tailed)	0.72	0.91	0.96	0.98	-	-	-	-	-	-	-	0.73
Commend NB	Kolmo-Smirnov	0.49	-	-	-	-	-	-	0.36	-	-	-	0.51
	Sig. (2-tailed)	0.97	-	-	-	-	-	-	1.00	-	-	-	0.96
Heraenium NA	Kolmo-Smirnov	0.73	-	-	-	-	-	-	0.72	-	-	-	0.44
	Sig. (2-tailed)	0.66	-	-	-	-	-	-	0.67	-	-	-	0.99
Noritake EX-3 (P)	Kolmo-Smirnov	0.65	-	0.61	-	-	-	-	0.52	0.44	-	-	0.44
	Sig. (2-tailed)	0.80	-	0.84	-	-	-	-	0.95	0.99	-	-	0.99
d-sign 30 (P)	Kolmo-Smirnov	-	0.52	-	-	-	-	-	0.39	-	-	-	0.39
	Sig. (2-tailed)	-	0.95	-	-	-	-	-	1.00	-	-	-	1.00
4-All (P)	Kolmo-Smirnov	0.61	-	-	-	-	-	-	0.55	-	-	-	0.57
	Sig. (2-tailed)	0.85	-	-	-	-	-	-	0.92	-	-	-	0.90
NNB (P)	Kolmo-Smirnov	0.67	-	0.71	-	-	-	-	-	0.78	-	-	0.60
	Sig. (2-tailed)	0.76	-	0.70	-	-	-	-	-	0.58	-	-	0.87
Discovery (P)	Kolmo-Smirnov	-	0.47	-	-	-	-	-	0.93	-	-	-	0.58
	Sig. (2-tailed)	-	0.98	-	-	-	-	-	0.35	-	-	-	0.88

(-) The distribution has no variance for this variable. One-Sample Kolmogorov-Smirnov Z Test cannot be performed.

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Appendix C

Comparison of element released to proposed proportion of metal compositions

Alloy (mean total released)	Ni composition	proposed Ni release	actual mean Ni released	CO composition	proposed Co release	actual mean Co released	CR composition	proposed Cr release	actual mean Cr released
Unpolished condition									
Commend (1623.01)	77.00	1249.72	509.71	-	-	-	14.00	227.22	40.27
Commend NB (25.13)	67.00	16.84	8.81	-	-	-	21.00	5.28	-
Heraenium NA (135.59)	59.30	80.40	11.85	-	-	-	24.00	32.54	-
Noritake EX-3 (251.40)	62.80	157.88	181.31	-	-	-	19.10	48.02	66.22
d-sign 30 (73.48)	-	-	-	60.20	44.24	49.44	30.10	22.12	24.05
4-All (290.50)	61.40	178.37	2.25	-	-	-	25.70	74.66	-
NNB (2426.82)	73.00	1771.58	739.64	-	-	-	12.00	291.22	104.83
Discovery (23.22)	-	-	-	59.50	13.82	4.75	31.50	7.31	-
Polished condition									
Commend (503.42)	77.00	387.63	402.52	-	-	-	14.00	70.48	50.74
Commend NB (18.46)	67.00	12.37	1.79	-	-	-	21.00	3.88	-
Heraenium NA (16.65)	59.30	9.87	1.08	-	-	-	24.00	4.00	-
Noritake EX-3 (94.39)	62.80	59.28	44.43	-	-	-	19.10	18.03	19.54
d-sign 30 (16.98)	-	-	-	60.20	10.22	2.42	30.10	5.11	-
4-All (15.51)	61.40	9.53	1.45	-	-	-	25.70	3.99	-
NNB (500.55)	73.00	365.40	429.50	-	-	-	12.00	60.07	67.79
Discovery (15.25)	-	-	-	59.50	9.08	1.04	31.50	4.80	-

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Appendix E

Multiple comparisons of mean total elements released from unpolished alloys

Dependent Variable: TOTAL

Tamhane

(I) GROUP	(J) GROUP	Mean Diff (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower	Upper
Commend	Commend NB	1597.880	35.962	0.000	1382.962	1812.797
	Heraenium NA	1487.420	36.588	0.000	1279.351	1695.490
	Noritake EX-3	1371.609	41.134	0.000	1182.184	1561.033
	d-sign 30	1549.523	36.123	0.000	1336.528	1762.518
	4-All	1332.509	38.268	0.000	1136.264	1528.754
	NNB	-803.815	80.560	0.000	-1186.645	-420.985
	Discovery	1599.789	35.923	0.000	1384.392	1815.185
Commend NB	Commend	-1597.880	35.962	0.000	-1812.797	-1382.962
	Heraenium NA	-110.459	7.439	0.000	-149.998	-70.921
	Noritake EX-3	-226.271	20.215	0.002	-345.572	-106.970
	d-sign 30	-48.357	4.639	0.000	-69.858	-26.856
	4-All	-265.371	13.457	0.000	-343.030	-187.712
	NNB	-2401.694	72.156	0.000	-2834.834	-1968.555
	Discovery	1.909	2.668	1.000	-9.879	13.697
Heraenium NA	Commend	-1487.420	36.588	0.000	-1695.490	-1279.351
	Commend NB	110.459	7.439	0.000	70.921	149.998
	Noritake EX-3	-115.812	21.309	0.039	-226.234	-5.389
	d-sign 30	62.102	8.183	0.002	24.654	99.551
	4-All	-154.911	15.051	0.000	-225.063	-84.760
	NNB	-2291.235	72.471	0.000	-2720.551	-1861.919
	Discovery	112.368	7.250	0.000	71.347	153.389
Noritake EX-3	Commend	-1371.609	41.134	0.000	-1561.033	-1182.184
	Commend NB	226.271	20.215	0.002	106.970	345.572
	Heraenium NA	115.812	21.309	0.039	5.389	226.234
	d-sign 30	177.914	20.501	0.006	61.625	294.204
	4-All	-39.100	24.080	0.985	-145.555	67.356
	NNB	-2175.423	74.869	0.000	-2582.034	-1768.813
	Discovery	228.180	20.146	0.002	108.062	348.299
d-sign 30	Commend	-1549.523	36.123	0.000	-1762.518	-1336.528
	Commend NB	48.357	4.639	0.000	26.856	69.858
	Heraenium NA	-62.102	8.183	0.002	-99.551	-24.654
	Noritake EX-3	-177.914	20.501	0.006	-294.204	-61.625
	4-All	-217.014	13.882	0.000	-291.102	-142.926
	NNB	-2353.338	72.237	0.000	-2785.476	-1921.200
	Discovery	50.266	4.329	0.000	27.952	72.579
4-All	Commend	-1332.509	38.268	0.000	-1528.754	-1136.264
	Commend NB	265.371	13.457	0.000	187.712	343.030
	Heraenium NA	154.911	15.051	0.000	84.760	225.063
	Noritake EX-3	39.100	24.080	0.985	-67.356	145.555
	d-sign 30	217.014	13.882	0.000	142.926	291.102
	NNB	-2136.324	73.333	0.000	-2556.243	-1716.404
	Discovery	267.280	13.353	0.000	188.481	346.078
NNB	Commend	803.815	80.560	0.000	420.985	1186.645
	Commend NB	2401.694	72.156	0.000	1968.555	2834.834
	Heraenium NA	2291.235	72.471	0.000	1861.919	2720.551
	Noritake EX-3	2175.423	74.869	0.000	1768.813	2582.034
	d-sign 30	2353.338	72.237	0.000	1921.200	2785.476
	4-All	2136.324	73.333	0.000	1716.404	2556.243
	Discovery	2403.603	72.137	0.000	1970.222	2836.985
Discovery	Commend	-1599.789	35.923	0.000	-1815.185	-1384.392
	Commend NB	-1.909	2.668	1.000	-13.697	9.879
	Heraenium NA	-112.368	7.250	0.000	-153.389	-71.347
	Noritake EX-3	-228.180	20.146	0.002	-348.299	-108.062
	d-sign 30	-50.266	4.329	0.000	-72.579	-27.952
	4-All	-267.280	13.353	0.000	-346.078	-188.481
	NNB	-2403.603	72.137	0.000	-2836.985	-1970.222

Appendix F

Multiple comparisons of mean total elements released from polished alloys

Tamhane

(I) GROUP	(J) GROUP	Mean Diff (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower	Upper
Commend (P)	Commend NB (P)	484.966	15.466	0.000	393.498	576.433
	Heraenium NA (P)	486.774	15.450	0.000	395.115	578.433
	Noritake EX-3 (P)	409.032	16.225	0.000	323.991	494.073
	d-sign 30 (P)	486.446	15.417	0.000	394.392	578.500
	4-All (P)	487.908	15.392	0.000	395.535	580.280
	NNB (P)	2.869	18.815	1.000	-79.184	84.921
	Discovery (P)	488.167	15.390	0.000	395.768	580.567
Commend NB (P)	Commend (P)	-484.966	15.466	0.000	-576.433	-393.498
	Heraenium NA (P)	1.809	2.151	1.000	-7.260	10.877
	Noritake EX-3 (P)	-75.934	5.402	0.000	-104.698	-47.169
	d-sign 30 (P)	1.480	1.901	1.000	-6.986	9.946
	4-All (P)	2.942	1.680	0.980	-5.963	11.847
	NNB (P)	-482.097	10.951	0.000	-545.842	-418.352
	Discovery (P)	3.202	1.660	0.954	-5.839	12.243
Heraenium NA (P)	Commend (P)	-486.774	15.450	0.000	-578.433	-395.115
	Commend NB (P)	-1.809	2.151	1.000	-10.877	7.260
	Noritake EX-3 (P)	-77.742	5.355	0.000	-106.831	-48.654
	d-sign 30 (P)	-0.328	1.765	1.000	-8.004	7.348
	4-All (P)	1.134	1.524	1.000	-6.758	9.025
	NNB (P)	-483.905	10.928	0.000	-547.903	-419.908
	Discovery (P)	1.393	1.502	1.000	-6.628	9.415
Noritake EX-3 (P)	Commend (P)	-409.032	16.225	0.000	-494.073	-323.991
	Commend NB (P)	75.934	5.402	0.000	47.169	104.698
	Heraenium NA (P)	77.742	5.355	0.000	48.654	106.831
	d-sign 30 (P)	77.414	5.260	0.000	47.515	107.312
	4-All (P)	78.876	5.184	0.001	48.166	109.585
	NNB (P)	-406.163	11.999	0.000	-463.863	-348.464
	Discovery (P)	79.135	5.178	0.001	48.350	109.921
d-sign 30 (P)	Commend (P)	-486.446	15.417	0.000	-578.500	-394.392
	Commend NB (P)	-1.480	1.901	1.000	-9.946	6.986
	Heraenium NA (P)	0.328	1.765	1.000	-7.348	8.004
	Noritake EX-3 (P)	-77.414	5.260	0.000	-107.312	-47.515
	4-All (P)	1.462	1.145	1.000	-3.981	6.905
	NNB (P)	-483.577	10.882	0.000	-548.110	-419.044
	Discovery (P)	1.722	1.115	0.994	-3.794	7.238
4-All (P)	Commend (P)	-487.908	15.392	0.000	-580.280	-395.535
	Commend NB (P)	-2.942	1.680	0.980	-11.847	5.963
	Heraenium NA (P)	-1.134	1.524	1.000	-9.025	6.758
	Noritake EX-3 (P)	-78.876	5.184	0.001	-109.585	-48.166
	d-sign 30 (P)	-1.462	1.145	1.000	-6.905	3.981
	NNB (P)	-485.039	10.845	0.000	-550.015	-420.063
	Discovery (P)	0.260	0.672	1.000	-2.584	3.103
NNB (P)	Commend (P)	-2.869	18.815	1.000	-84.921	79.184
	Commend NB (P)	482.097	10.951	0.000	418.352	545.842
	Heraenium NA (P)	483.905	10.928	0.000	419.908	547.903
	Noritake EX-3 (P)	406.163	11.999	0.000	348.464	463.863
	d-sign 30 (P)	483.577	10.882	0.000	419.044	548.110
	4-All (P)	485.039	10.845	0.000	420.063	550.015
	Discovery (P)	485.299	10.842	0.000	420.285	550.313
Discovery (P)	Commend (P)	-488.167	15.390	0.000	-580.567	-395.768
	Commend NB (P)	-3.202	1.660	0.954	-12.243	5.839
	Heraenium NA (P)	-1.393	1.502	1.000	-9.415	6.628
	Noritake EX-3 (P)	-79.135	5.178	0.001	-109.921	-48.350
	d-sign 30 (P)	-1.722	1.115	0.994	-7.238	3.794
	4-All (P)	-0.260	0.672	1.000	-3.103	2.584
	NNB (P)	-485.299	10.842	0.000	-550.313	-420.285

CURRICULUM VITAE

Miss Kasree Chiewcharnvalijkit was born on July 22, 1978, in Nakhon Pathom, Thailand. Kasree graduated from Chiang Mai University in 2002 with an honors degree in Dental Surgery (D.D.S.). She was employed as a member of the teaching staff in the Faculty of Dentistry at Thammasat University. In the following year 2003, she enrolled in the "Master of Science program in Prosthodontics" in Chulalongkorn University.

In year 2001, Miss Chiewcharnvalijkit won a Thai student award for the International Association of Student Clinicians-American Dental Association (SCADA). In 2003, Kasree proudly represented Thailand at the Student Clinician Program in Hong Kong at Dentsply/IADR SEA (International Association of Dental Research, South-East Asia Division). She attended and took part in the Asian Academy of Prosthodontics as an organizing committee member in 2005.

In the present time, she is engaged as a dental practitioner and as a Prosthodontist in a private dental clinic. Kasree is an active member in the Thai Dental Association, the International Association of Student Clinicians-American Dental Association (SCADA) and the Thai Prosthodontics Association.

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