

Ion release from metal-ceramic alloys in three different media

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The aim of this *in vitro* study was to assess the effect of pH changes on ion release of metal-ceramic dental casting alloys. Samples from four commercially available alloys (Wirobond C, Wiron 99, Rematitan CP-Ti grade 1, and PontoStar) were prepared and polished. Ion release of alloys subjected to three different pH media (artificial saliva of pH 2.3, pH 6.5 and 0.9% saline solution of pH 7.3) for periods of 7, 15, 30, and 60 days were assessed by means of atomic absorption spectroscopy. Microscopic changes on surfaces of metallic samples before and after immersion were compared by scanning electron microscopy. ANOVA was used for statistical analysis of results. For all ions, pH and period interactions were statistically significant: highest amount of ion release occurred after 60 days of immersion regardless of pH value. For every alloy, ion release results were highest in artificial saliva of pH 2.3 and lowest in 0.9% saline solution. It was concluded that ion release from alloys was pH-dependent.

Keywords: Metal-ceramic alloys, Ion release, Corrosion, pH changes

INTRODUCTION

Biocompatibility and corrosion resistance of metal-ceramic alloys are closely interconnected. The toxicity of metal-ceramic alloys depends on various aspects of the metal ions released due to corrosion: quality and quantity of released ions, eventual synergistic or antagonistic effects of released ions, and the length of time they remain in contact with organic tissues¹. Ions released during corrosion may be detectable by the patient as a shock that can be disconcerting and even debilitating. Released metallic components may also cause an undesirable metallic taste. Given these unpleasant circumstances, the patient may request for the restoration to be removed.

Many factors contribute to the corrosion of metallic restorations—from inherent properties of the metal used to the environmental factors in the oral cavity. Factors inherent in the metal used include its microstructure, chemical composition, construction technique, and even its galvanic contacts with other existing metallic restorations. On the environmental factors, the oral cavity is a conducive medium for corrosion. Factors that may initiate corrosion include the quantity, quality, and pH value of secreted saliva (which are affected by the diet and intake of medicines or drugs), intake of organic acids commonly found in foods and beverages (such as lactic, acetic, malic, oxalic, tartaric, and carbonic acids), temperature fluctuations due to food and drink intake, and accumulation of dental plaque (formed by a combination of acids, bacteria, saliva, and food remnants).

Many studies have reported on the release of metallic ions from high-noble, noble, and base dental casting alloys under differing pH conditions which simulated the oral cavity^{2,3}. A low pH environment (*i.e.*,

acidic conditions) increases the release of metallic ions from dental alloys. This effect is especially pronounced for nickel (Ni)-based alloys^{4,5}. Dental plaque often adheres to dental alloys and creates a low pH environment locally. This condition promotes the corrosion of dental alloys, thereby causing concern about the biocompatibility of dental alloys⁶.

The corrosion resistance of an alloy is of fundamental importance to its biocompatibility. The release of ions from the alloy is nearly always necessary for adverse biologic effects such as toxicity, allergy, or mutagenicity⁶. Elevated levels of corrosion products released in the oral biological environment may cause pathological reactions in the gastrointestinal system or surrounding tissues⁷. Hence, from biocompatibility standpoint, the most relevant measure of corrosion is identifying and quantifying the ions that are released. Elements such as beryllium (Be), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), palladium (Pd), and vanadium (V) are known to be toxic, allergic, or mutagenic, and they should be used in lower ratios in dental alloys⁶.

Several studies have measured the release of metallic ions from dental alloys of different alloy compositions^{1,4,6,8-10}. For many Ni-based dental casting alloys, Ni was the main element released while other major elements (Cr and molybdenum (Mo)), which are considered less toxic, were released at much lower concentrations⁸. In commercial alloys, the compositions of Cr and Mo range from 11 to 25 wt% and 0 to 10 wt% respectively. In a recently published study⁹, it was reported that the total amount of Cr and Mo within the alloys proved to be of greater influence on corrosion resistance. Alloys that contained lower amounts of Cr and Mo were reportedly more susceptible to corrosion^{5,11}. A higher amount of chromium (25 wt%) would result in

superior corrosion resistance, and this was associated with a more uniform distribution of Cr in the alloy microstructure¹¹. Conversely, if Cr content was less than 16–20 wt%, Ni release increased under all conditions (*i.e.*, both acidic and alkaline)¹².

Noble metals are known to be resistant to corrosion. Studies have shown that dental alloys which contained less than 50% of noble metals exhibited tarnish and corrosion^{2,13}. Therefore, biological risks can be kept to a minimum with the use of high-noble and noble alloys because ion release from these alloys is lower^{1,2,10,13–15}. Nonetheless, there were conflicting reports on ion release behavior from noble alloys in low pH conditions, which could be attributed to differences of the environment surrounding the tested alloys¹². On one hand, it was reported that low pH caused ion release from Au alloy to increase; on the other hand, it was also reported that noble alloys were not significantly affected by a low pH^{10,12}.

Titanium (Ti) and its alloys have become one of the backbone materials for many applications today because of their combination of high strength-to-weight ratio, excellent mechanical properties, and corrosion resistance. Moreover, because of its high reactivity, a surface oxide layer is formed during the casting and soldering of pure Ti. It is widely reported that the excellent biocompatibility of Ti and its alloys is closely related to the surface oxide layer. In dentistry, Ti is used for crowns and bridges, dental implants, and denture frameworks because of its excellent biocompatibility. Although Ti and its alloys are hypoallergenic and possess many of the clinically favored properties of type III and type IV Au dental alloys, their use is largely limited by their relatively high cost¹⁶.

Ion release from dental alloys has been evaluated mainly by *in vitro* studies using these methods: cell culture media^{1,8,15,17}, galvanism¹⁸, electrolyte baths¹⁹, evaluation of the influence of oral proteins on corrosion behavior^{2,20}, exposure to different pH levels^{2,3,5,10,20,21}, use of different surface treatments to cast alloys^{9,13}, and power toothbrushing with toothpastes of different abrasivities²². In general, a static system is the most

frequently used method to monitor the elements released from dental casting alloys. To measure even a low corrosion rate, *in vitro* electrochemical techniques have proved to be sufficiently sensitive to fulfill this task; moreover, they are quick and convenient and are now used by many researchers⁷. There are two types of electrochemical techniques. The first involves immersion testing with analytical determination of the quantity of released metal ions by atomic absorption spectroscopy (AAS) or inductively coupled plasma spectroscopy (ICPS). The second involves potentiodynamic and potentiostatic polarization measurements to evaluate corrosion behavior.

To date, only a few studies have investigated the effect of pH on ion release from high-noble alloys and Ti alloys. The aim of this study was to evaluate the release of ions from four commercially available dental casting alloys in three different pH media —artificial saliva of pH 2.3 and pH 6.5 and 0.9% saline solution of pH 7.3 — for a period of 60 days. A Co-Cr based alloy, a Ni-Cr-based alloy, a Ti-based alloy, and a high-Au alloy were selected for this study. The corrosion products, namely the released ions, were identified and quantified using AAS. Microscopic changes on the surfaces of the alloy samples were observed using scanning electron microscopy (SEM) before and after immersion in different pH media.

MATERIALS AND METHODS

Preparation of alloy samples

Four commercially available metal-ceramic dental casting alloys representing different compositions were selected for this study (Table 1): a Co-Cr-based alloy (Wirobond C, Bego, Bremen, Germany; WBC), a Ni-Cr-based alloy (Wiron 99, Bego, W99), a Ti-based alloy (Rematitan CP-Ti grade 1, Dentaaurum, Pforzheim, Germany; RTI), and a high-Au alloy (PontoStar, Bego; PSR).

Carried out as per the manufacturers' recommendations, WBC, W99, and PSR alloys were cast into disks of 3 mm diameter and 2 mm thickness ($n=8$ per alloy) and polished. For RTI alloy, disk samples of

Table 1 Metal-ceramic alloys assessed in the study

Material/Product name	Code	Manufacturer	Lot number	Composition (wt%)
Co-Cr-Mo-based alloy Wirobond C (color: white)	WBC	Bego-Germany	1967	61 Co, 26 Cr, 6 Mo, 5 W, 1 Si, 0.5 Fe, 0.5 Ce, 0.02 C
Ni-Cr-Mo-based alloy Wiron 99 (type 4, color: white)	W99	Bego-Germany	9868	65 Ni, 22.5 Cr, 9.5 Mo, 1 Si, 1 Nb, 0.5 Fe, 0.5 C
Ti-based alloy Rematitan CP-Ti grade 1	RTI	Dentaaurum-Germany	148	99.49 Ti, 0.15 Fe, 0.12 O, 0.06 C, 0.05 N
High-Au alloy PontoStar (type hard 3, color: gold yellow)	PSR	Bego-Germany	941901	85 Au, 11.6 Pt, 1.5 In, 1.3 Rh, 0.6 Pd

the same dimensions ($n=8$) were prepared and polished in the Metallurgy Laboratory of Research and Development Department of Dentaurem. To ensure sample homogeneity, the diameter ($R=3\pm 0.1$ mm) and height ($h=2\pm 0.1$ mm) of each sample were checked using a caliper compass. With a precision scale, sample weights were determined as follows: 0.355 ± 0.050 g for WBC, 0.350 ± 0.050 g for W99, 0.180 ± 0.020 g for RTI, and 0.330 ± 0.030 g for PSR.

Immersion solutions

Three test solutions (Table 2) were used in this study for immersion testing before AAS and SEM analyses: artificial saliva with pH 2.3 (AS-LA) and pH 6.5 (AS-SS), and 0.9% saline solution at pH 7.3 (SS).

1. Artificial saliva media with pH 2.3 and pH 6.5

To prepare artificial saliva, 7.69 g of K_2HPO_4 , 2.46 g of KH_2PO_4 , 5.3 g of NaCl, and 9.3 g of KCl were added to 1,000 mL of distilled water. The prepared solution was divided into two balloon glasses equally.

According to ISO 10271:2001 Standard²³, the pH of solution used for immersion testing should be acidic (2.3 ± 0.1). Moreover, dental plaque produces a reduced pH, making it more relevant to test the effects of acids on dental alloys to address the biocompatibility concerns⁶. Average salivary pH is 6.7. The pH of artificial saliva was lowered to 2.3 by adding lactic acid (to obtain AS-LA) and to 6.5 by adding NaOH (to obtain AS-SS). After the pH values were adjusted to their desired levels using lactic acid and NaOH, they were measured using a pH meter (Philips PW 9422). The AS-LA solution was used to test the extreme conditions of short-term pH variances. Examples of causes of short-term pH variances include the intake of acidic beverages. The AS-SS solution was

used to test pH variances arising from long-term exposure, such as that of daily saliva.

2. Saline solution with pH 7.3

0.9% NaCl saline solution with pH 7.3 was coded as SS solution in this study. Its chloride (Cl) concentration was very similar to that of human body fluid. It was thus used as a control.

Immersion test

After 10 mL of each test solution was poured into coded polypropylene test tubes, they were mixed and homogenized using a vibrator (NM-110 Vortex). Metal samples were coded, washed in distilled water and alcohol, and then immersed in polypropylene tubes containing the immersion solutions. To monitor the release of metallic ions into the immersion solutions in polypropylene tubes, control test tubes containing immersion solutions only were also prepared. All test tubes were incubated at 37°C. No pH measurements were carried out during immersion test procedures to avoid disturbing the ion release process.

There is a close link between the conditions under which experiments are performed and the eventual experimental results. For this reason, special care was exercised when preparing the immersion solutions, and in particular the composition of the immersion solution²⁴.

Atomic absorption spectroscopy

After 7, 15, 30, and 60 days of immersion, the quantities of metallic ions released were measured by AAS. This technique is able to quantify metal ions in very dilute concentrations in the range of parts per billions (ng/mL). For a few seconds every day, a vortex was used to mix the immersion solutions in all the test tubes. After

Table 2 Artificially prepared solutions used for immersion

Solution	Code	pH	Composition (mL)
Artificial saliva + lactic acid	AS-LA	2.3	12 mL lactic acid to 500 mL solution
Artificial saliva + 0.9%NaCl	AS-SS	6.5	(0.126 g NaOH + 0.9% NaCl) to 500 mL solution
Saline solution (0.9%NaCl)	SS	7.3	0.9% NaCl

Table 3 Atomic absorption spectroscopy parameters used for the elements

Element	Wavelength (nm)	Slit Width (nm)	Lamp Current (mA)	Flame*
Au	242.8	0.7	4	–
Co	240.7	0.2	7	–
Cr	357.9	0.2	7	–
Fe	248.3	0.2	5	A/A
In	303.9	0.5	5	–
Mo	313.3	0.5	7	–
Ni	341.5	0.2	4	–
Pt	265.9	0.2	10	–
Ti	365.4	0.2	20	–

* A/A = air/acetylene

mixing, 2 mL of immersion solution was removed from each test tube and Au, Pt, In, Cr, Co, Mo, Fe, Ti, and Ni ion levels were measured using an AAS (Varian 30/40, Varian Techtron Pty Ltd., Mulgrave, Victoria, Australia).

AAS uses absorption of light to measure the concentration of atoms in the gas phase. Ions or atoms in a sample must be dissolved and vaporized in a high-temperature source such as a flame or graphite furnace. Flame AA can analyze solutions only, while graphite furnace AA can accept solutions, slurries, or solid samples. Flame AA needs a slot-type burner to increase the path length to increase the total absorbance. Sample solutions are usually aspirated with the gas flow into a nebulizing/mixing chamber to form small droplets before entering the flame. Compared to flame AA, the graphite furnace yields several advantages. It is a more efficient atomizer than a flame and it can directly accept very tiny absolute quantities of samples. After a sample is placed directly in the graphite furnace, the furnace is electrically heated in several steps to dry the sample, ash organic matter, and vaporize the analyte atoms.

In this study, Fe ions were measured using flame AA method, while the other ions (Au, Pt, In, Cr, Co, Mo, Ti, and Ni ions) were measured using the graphite furnace AA method. Table 3 lists the specific parameters used for the detection of each element. Analysis for each sample was carried out in triplicate and the value obtained by calculating the average of three experiments.

Scanning electron microscopy

The surface appearances of the polished disk samples before immersion and the microscopic changes that occurred after 60 days of immersion were examined by SEM (JSM 6400, Jeol, Tokyo, Japan). Samples randomly selected from each group were washed under distilled water and observed under these SEM settings: 20 kV accelerating potential and $\times 1,000$ magnification.

Statistical analysis and comparison of results

Statistical analysis for periods was performed using one-way ANOVA. Repeated-measures ANOVA and independent t-test were also used to evaluate the effect of immersion period. To make comparisons with previous studies, percent compositions of metal ion corrosion products released from the metal-ceramic alloys were also calculated.

Ion release concentrations obtained from atomic absorption measurements were expressed in ng/mL. According to ISO 8891:1998²⁵⁾, the maximum quantity of released corrosion products was allowed to be $100 \mu\text{g}/\text{cm}^2$ per week. To calculate ion release in $\mu\text{g}/\text{cm}^2$ for each metal-ceramic alloy in three different media for a period of 7 days, amounts in ng/mL were converted to μg of mass released from the alloy per square centimeter of alloy surface exposed to the immersion solution for each ion.

RESULTS

When a dental alloy is placed in the oral environment, it is subjected to chemical attacks and consequently releases metallic ions into the oral environment. In this study, three artificially prepared solutions mimicked the pH variances routinely encountered in the oral environment. Four dental alloys representing different compositions were immersed in these solutions for a 60-day period. AAS was used to measure the concentration levels of different metallic ions released from the dental alloys into the immersion solutions. No alloy samples were removed from the immersion solutions throughout the entire 60-day period; only solution samples were removed from the test tubes at every designated time period.

AAS analysis

Figures 1–4 show the results of released ions from the four dental alloys in three different media over a 60-day

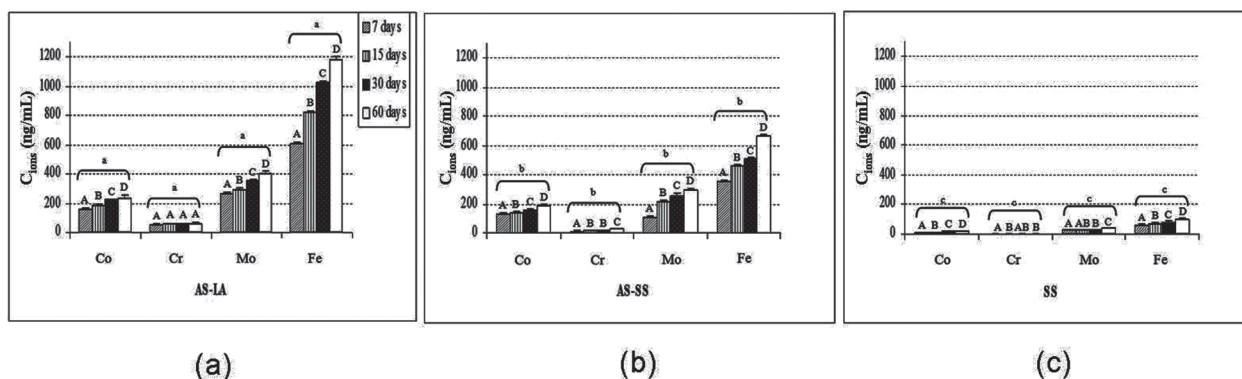


Fig. 1 Release amounts of Co, Cr, Mo, and Fe elements from WBC alloy in: (a) AS-LA solution; (b) AS-SS solution; and (c) SS solution. Error bar indicates one standard deviation of $n=8$. A, B, C, D: Capital letters indicate statistically significant differences in release amount of an immersion group among the periods ($p < 0.05$). a, b, c: Small letters indicate statistically significant differences among immersion period solutions in each time period ($p < 0.05$).

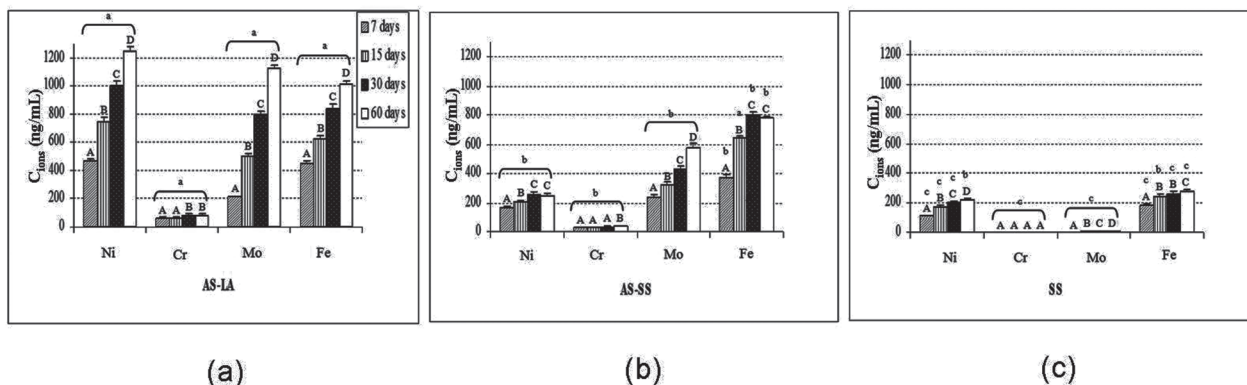


Fig. 2 Release amounts of Ni, Cr, Mo, and Fe elements from W99 alloy in: (a) AS-LA solution; (b) AS-SS solution; and (c) SS solution. Error bar indicates one standard deviation of $n=8$. A, B, C, D: Capital letters indicate statistically significant differences in release amount of an immersion group among the periods ($p<0.05$). a, b, c: Small letters indicate statistically significant differences among immersion solutions in each time period ($p<0.05$).

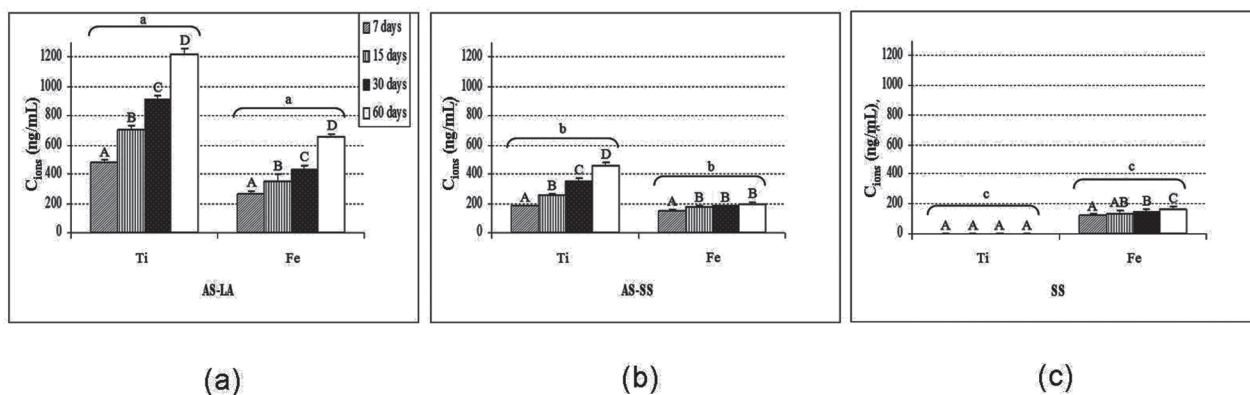


Fig. 3 Releases amounts of Ti and Fe elements from RTI alloy in: (a) AS-LA solution; (b) AS-SS solution; and (c) SS solution. Error bar indicates one standard deviation of $n=8$. A, B, C, D: Capital letters indicate statistically significant differences in release amount of an immersion group among the periods ($p<0.05$). a, b, c: Small letters indicate statistically significant differences among immersion solutions in each time period ($p<0.05$).

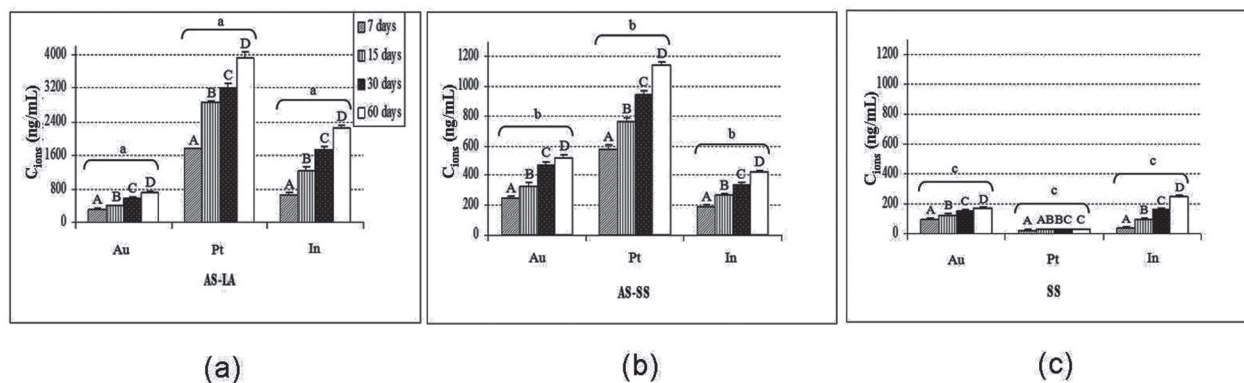


Fig. 4 Release amounts of Au, Pt, and In elements from PSR alloy in: (a) AS-LA solution; (b) AS-SS solution; and (c) SS solution. Error bar indicates one standard deviation of $n=8$. A, B, C, D: Capital letters indicate statistically significant differences in release amount of an immersion group among the periods ($p<0.05$). a, b, c: Small letters indicate statistically significant differences among immersion solutions in each time period ($p<0.05$).

period. For all the dental alloys in all the three media, ion concentration of each element increased toward the 60th day. This meant that the metallic ion release processes increased with length of immersion period, except for Ni ions of W99 alloy in AS-SS solution.

Statistical analysis revealed statistically significant interactions between pH of immersion medium and immersion period. For every immersion group, repeated-measures ANOVA was performed to evaluate the effect of immersion period. Different capital letters (A, B, C, or D) were shown in Figs. 1–4 to indicate presence of

statistically significant differences ($p < 0.05$) in ion release amount among the immersion periods for each immersion group. However, for all the periods, differences among the immersion groups were examined by one-way ANOVA and indicated with small letters (a, b, or c) for presence of statistically significant differences ($p < 0.05$) in Figs. 1–4.

Based on AAS measurements, Table 4 presents the percent compositions (wt%) of metal ion corrosion products released from each metal-ceramic alloy in each immersion medium after 60 days.

Table 4 Percent compositions (wt%) of metal ion corrosion products released from metal-ceramic alloys based on 60-day atomic absorption measurements in three different media

	Co	Cr	Mo	Fe	Ni	Ti	Au	Pt	In	TOTAL
Alloys in AS-LA										
WBC	0.66	0.16	1.12	3.32						5.26
W99		0.24	3.22	2.90	3.56					9.92
RTI				3.62		6.76				10.38
PSR							2.18	11.92	6.76	20.86
Alloys in AS-SS										
WBC	0.50	0.06	0.82	1.86						3.24
W99		0.10	1.64	2.24	0.68					4.66
RTI				1.06		2.54				3.60
PSR							1.54	3.46	1.26	6.26
Alloys in SS										
WBC	0.04	0.02	0.08	0.26						0.40
W99		0.00	0.02	0.78	0.60					1.40
RTI				0.92		0.00				0.92
PSR							0.52	0.08	0.74	1.34

Table 5 Average released quantity of elements from metal-ceramic alloys ($\mu\text{g}/\text{cm}^2$ week)

Alloys	Elements	in AS-LA	in AS-SS	in SS
WBC	Co	4.731	3.791	0.272
	Cr	1.516	0.424	0.090
	Mo	8.007	3.366	0.788
	Fe	18.289	10.646	1.759
	Total	32.543	18.227	2.909
W99	Ni	14.134	5.186	3.366
	Cr	1.728	0.788	0.000
	Mo	6.369	7.006	0.090
	Fe	13.557	11.191	5.641
	Total	35.788	24.171	9.097
RTI	Ti	14.649	5.489	0.000
	Fe	8.007	4.367	3.851
	Total	22.656	9.856	3.851
PSR	Au	9.493	7.521	2.972
	Pt	53.351	17.591	0.667
	In	19.836	5.823	1.243
	Total	82.680	30.935	4.882

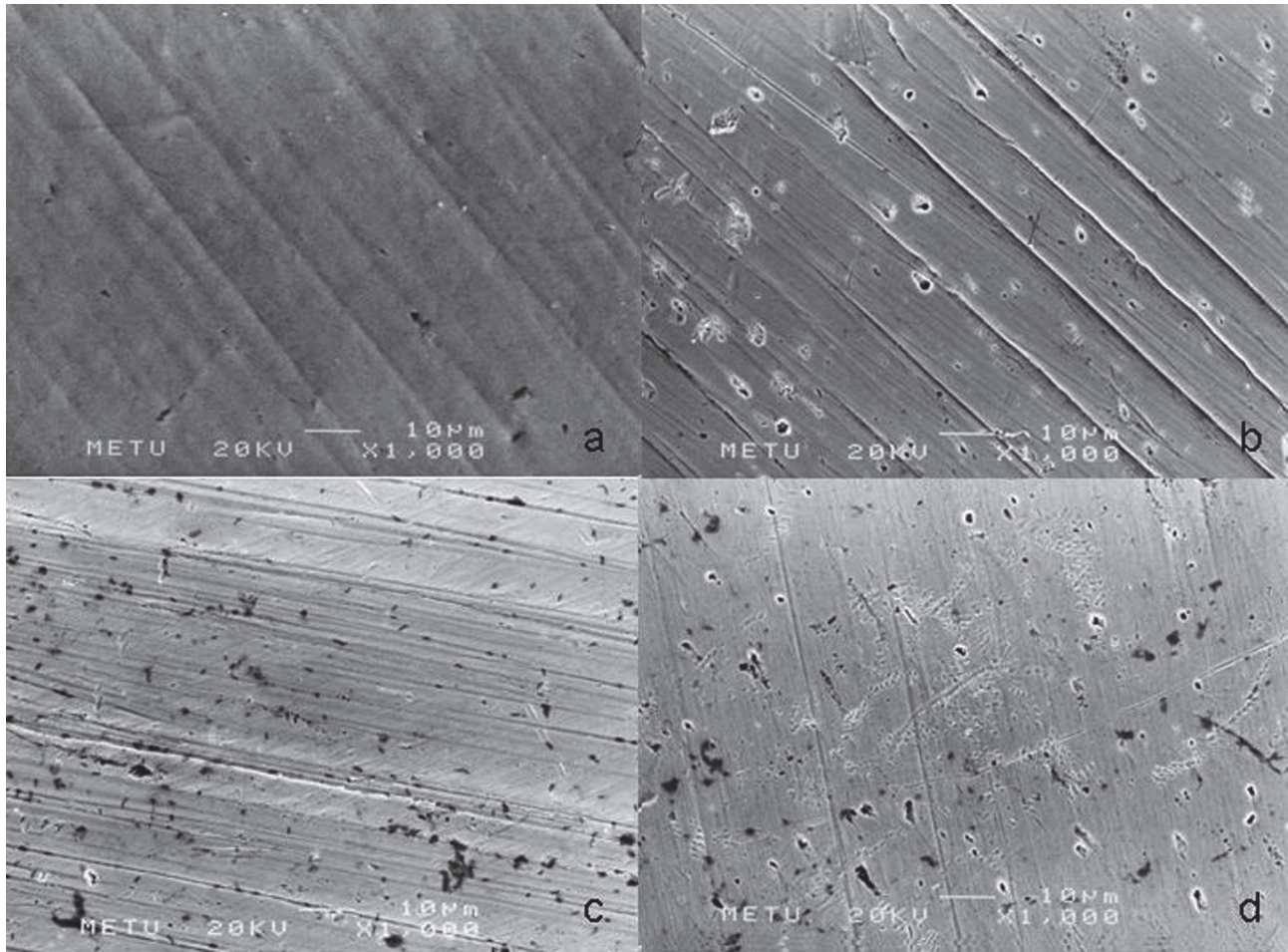


Fig. 5 SEM pictures of WBC alloy: (a) before immersion; (b) after immersion in AS-LA; (c) after immersion in AS-SS; and (d) after immersion in SS.

On ion release per week, ISO 8891:1998²⁵⁾ recommended that the maximum quantity released was allowed to be $100 \mu\text{g}/\text{cm}^2$ week. Three classes, classes I–III, have been defined based on the quantity released per week. Alloys in class I release $10 \mu\text{g}/\text{cm}^2$ week or less, alloys in class II $10\text{--}100 \mu\text{g}/\text{cm}^2$ week, and alloys in class III $100\text{--}1,000 \mu\text{g}/\text{cm}^2$ week. In this study, all dental casting alloys immersed in AS-LA solution belonged to class II (Table 5). Alloys WBC, W99, and PSR immersed in AS-SS solution also belonged to class II (Table 5). On the overall, none of the alloys released such a large quantity of metallic ions to induce adverse biological reactions.

SEM analysis

SEM micrographs of WBC, W99, RTI, and PSR alloys before immersion and after immersion in AS-LA, AS-SS, and SS are shown in Figs. 5–8 respectively. Surface corrosion was observed for all alloy samples, and in particular high acidic effect after immersion in AS-LA solution with pH 2.3. PSR alloy presented the smoothest surface micrographs.

DISCUSSION

Ion release and biocompatibility

In the oral environment, the biocompatibility of a dental casting alloy is inextricably linked to its ion release behavior. In living systems, some metals have biological functions. While Fe is essential in relatively high concentrations, other elements such as Zn, Cu, Ni, Co, Mo, and perhaps Cr, are essential in trace amounts for some living systems. At higher concentrations, they can become very toxic. Some metals such as mercury, lead, cadmium, and uranium have no clear biological functions and are toxic even at very low levels.

It is not realistic for all metal-ceramic alloys introduced on the market to be evaluated in both experimental and clinical studies. Clinical trials are time-consuming, expensive, and in some instances inappropriate or unethical. Laboratory tests are an attractive practical alternative in light of the positive correlation between laboratory tests and clinical trials. In this study, four commercially available metal-ceramic dental casting alloys representing different compositions

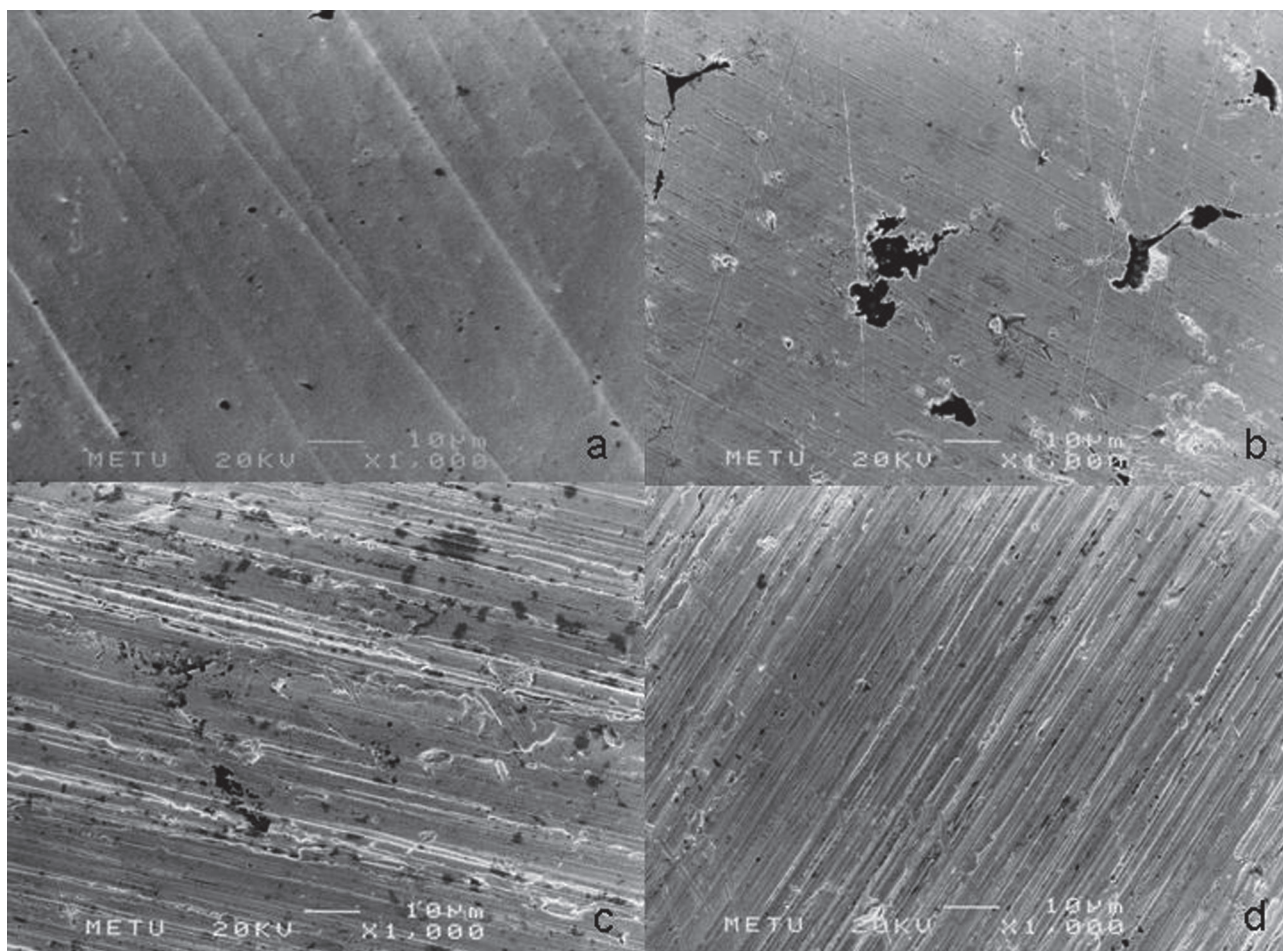


Fig. 6 SEM pictures of W99 alloy: (a) before immersion; (b) after immersion in AS-LA; (c) after immersion in AS-SS; and (d) after immersion in SS.

were selected: WBC (Co-Cr-based alloy), W99 (Ni-Cr-based alloy), RTI (Ti-based alloy), and PSR (high-Au alloy). For a fair assessment of the effect of chemical composition on corrosion resistance and metallic ion release, the four selected alloys were subjected to identical test conditions of being immersed in AS-LA, AS-SS, and SS for a period of 60 days. To simulate the oral temperature, all immersion solutions containing the alloy samples were incubated at 37°C.

Both nickel and chromium could cause hypersensitivity. Thus, the potential health hazards of these metals and their compounds have been the focus of attention for more than 100 years²⁶. According to Barrett *et al.*²⁷, the average dietary intake of Ni is 200–300 µg/day. The amount of Ni necessary to induce allergy after a single exposure has been calculated to be 0.6–2.5 mg⁴. In the present study, quantities of Ni released from Ni-based alloy W99 in the three different immersion media (Table 5) were markedly below the average dietary intake of 200–300 µg/day²⁶.

Chromium is an essential nutrient of man in amounts of 50–200 mg/day in glucose metabolism. The

average dietary intake of Cr is 280 µg/day²⁶. However, chromate salts—which result from the corrosion of base metal alloys—could cause skin sensitivity and dermatitis. Incidence of Cr allergy was reported to be 10% in males and 3% in females. The estimated lethal dose for Cr in humans is about 50–70 mg/kg body weight²⁶. In the present study, quantities of Cr released from WBC and W99 (Table 5) were also markedly below the average dietary intake of 280 µg/day²⁶.

Factors related to ion release

Intraoral corrosion is a very complex process. Factors that affect corrosion and metal ion release run the gamut from composition and metallurgical state, combinations within a construct, surface conditions, mechanical aspects of function, to the local and systemic host environment²⁸.

1. Chemical composition of alloy

Starting with an alloy's chemical composition, some alloying elements are known by their lability more than other elements. Some alloying combinations may result in synergistic effects which alter the elements' lability

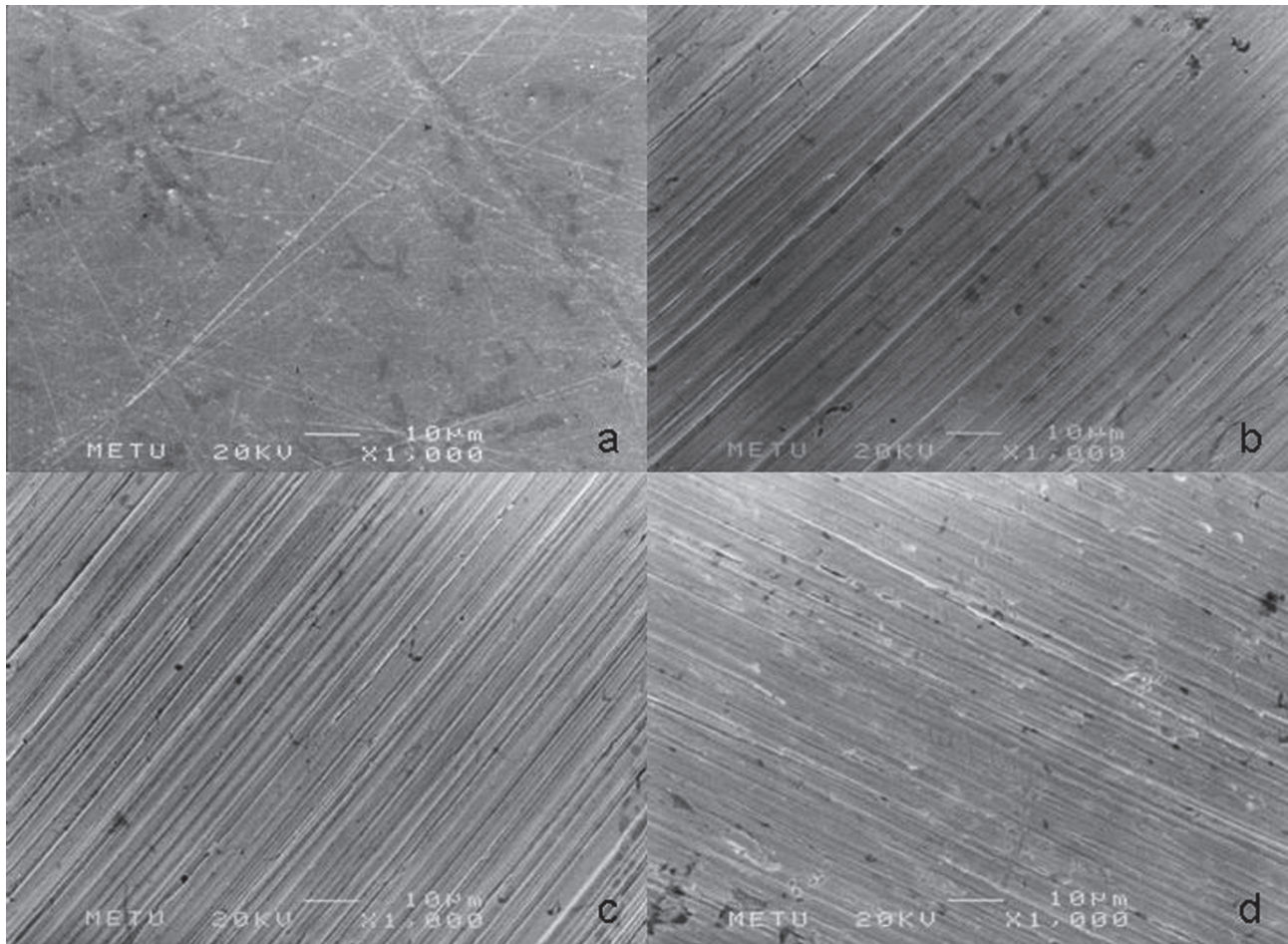


Fig. 7 SEM pictures of RTI alloy: (a) before immersion; (b) after immersion in AS-LA; (c) after immersion in AS-SS; and (d) after immersion in SS.

and thus increase or decrease the ion release rate^{2,3,5,6,22,28,29}). Ni, Cr, Mo, and Co had a decreasing effect on the corrosion rate of base metal alloys^{5,17,24,30-32}, whereas Fe had an increasing effect^{10,24}. The ion release results of WBC, W99, and RTI in the present study (Figs. 1–3) showed similar findings.

A survey of published literature showed that Cr, Mo, manganese (Mn), and tungsten (W) were alloy elements with strong beneficial influence on the corrosion resistance of Ni-based and/or Co-Cr alloys^{33,34}. Yfantis *et al.*³⁴ suggested that the enhanced corrosion behavior of WBC was due to W addition and its relatively high Cr content. Bilhan *et al.*³³ showed that Mo and Mn additions to Ni-based alloys improved their corrosion resistance, and that alloys with a high Mo content had better corrosion properties than those with a low level. Al-Hiyasat *et al.*³¹ reported that for ion release from Ni-Cr and Co-Cr alloys used in their study, Cr release was very low when compared with Mo and Ni ions; in most cases, Cr release was below the detection limit. Similarly, other studies have reported that Cr release was consistently low even in different immersion

solutions^{8,17,34}. In the present study, Cr release from WBC and W99 alloys was indeed very low in all immersion solutions, especially when compared with the release of Co, Mo, Fe, and Ni ions.

A survey of published literature also showed that an alloy was protected against corrosion when its Cr content was higher than 16 wt%^{5,22,30,32}. Pfeiffer *et al.*⁵ reported that when the content of Cr in an alloy was lower than 16 wt%, Ni release from the alloy became higher. However, when Cr content was above 20 wt%, Strietzel and Viohl³⁰ reported that the alloy exhibited long-term corrosion resistance. Molina *et al.*²² reported that a complex stable passive oxide layer which provided adequate corrosion resistance was formed on the surfaces of Ni-Cr alloys containing 16–22% Cr and 9–14% Mo; on the contrary, an Ni-Cr-Mo alloy with a low Cr and Mo content was associated with a high corrosion rate and susceptibility to accelerated corrosion processes. Similarly, Manaranche and Hornberger³² reported that when the content of Cr was more than 18 wt%, passivation of the alloy surface took place and the impervious passive film protected the alloy against corrosion. In the present

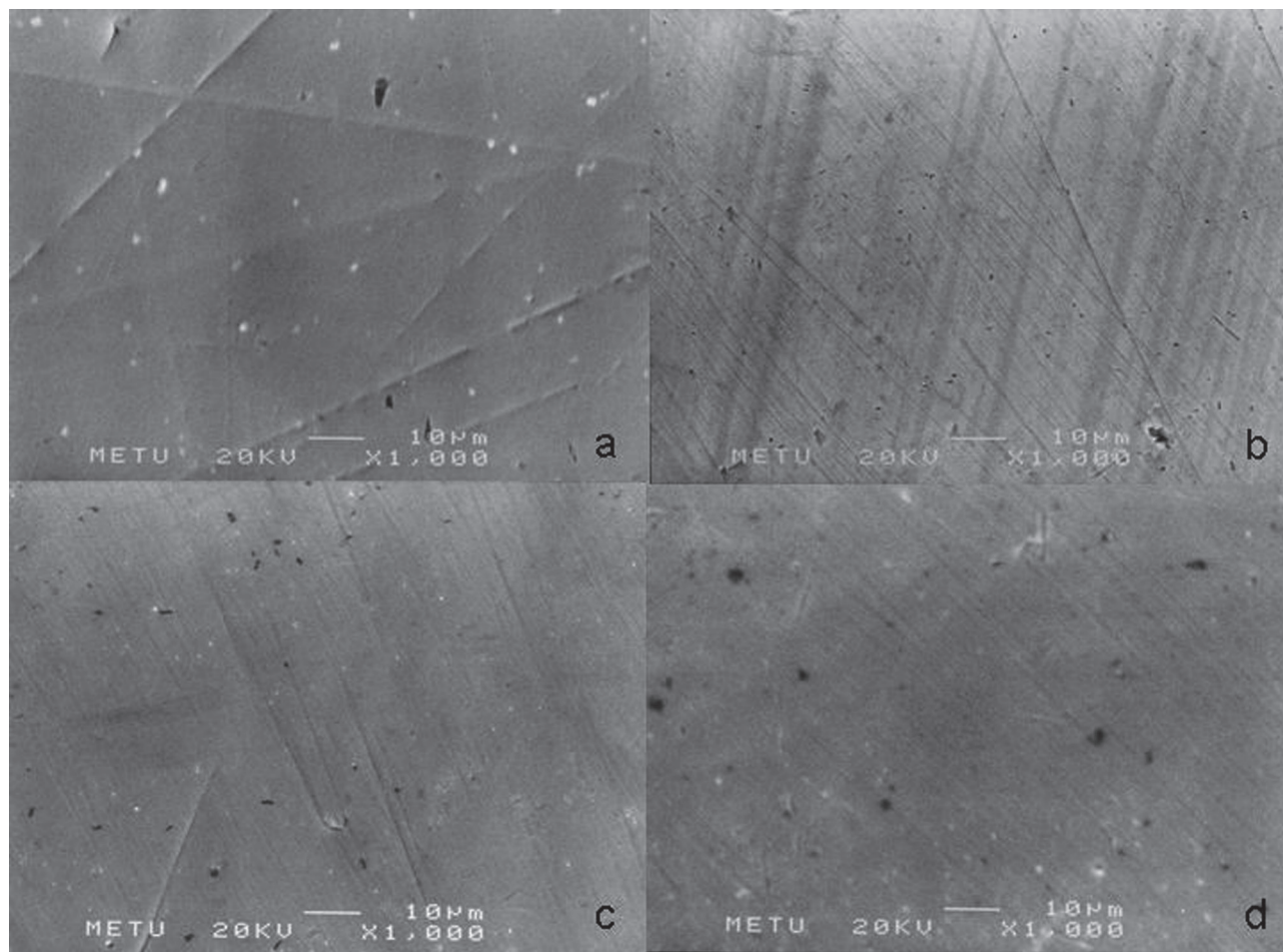


Fig. 8 SEM pictures of PSR alloy: (a) before immersion; (b) after immersion in AS-LA; (c) after immersion in AS-SS; and (d) after immersion in SS.

study, the contents of Cr in WBC and W99 were 26 wt% and 22.5 wt% respectively (Table 1). With a higher Cr content in WBC alloy, its corrosion resistance was expectedly higher than that of W99. As seen in Figs. 1–2 and Table 4, the release of Co and Mo ions from WBC alloy was lower than the release of Ni and Mo ions from W99 alloy.

Although Co-Cr based alloys are known to have excellent corrosion resistance^{4,34}, Reclaru *et al.*³⁵ reported that the presence of precious metals (Au, Pt, Ru) deteriorated the corrosion resistance of Co-Cr dental alloys in a significant way—a fitting and resounding indication of the influence of chemical composition on corrosion behavior.

2. Carbon content and microstructure

Of the three thermodynamically stable forms of chromium carbides, Cr_{23}C_6 is the most stable compound. Carbide stability is markedly temperature-dependent, with markedly higher concentrations of C and Cr formed in acidic environments. This means that in an acidic medium, Cr_{23}C_6 compound easily forms³⁶. However, if Cr_{23}C_6 is formed in the microstructures of Co-Cr and

Ni-Cr alloys in acidic media, then Cr is no longer available to provide corrosion resistance. This means that Cr_{23}C_6 formation must be prevented in dental casting alloys.

In WBC alloy, the content of C was 0.02 wt% (Table 1). Extra low C levels, preferably below 0.03 wt%, are a highly recommended means to prevent Cr_{23}C_6 formation in casting alloys. The theory is that carbides will not form if the C level is below some critical value. Nonetheless, some carbides still form at low C levels and in properly heat-treated materials, but they are few and far between.

In W99 alloy, where the content of C was 0.5 wt%, the use of carbon stabilizing elements such as niobium (Nb; 1 wt% in W99 alloy, Table 1) was the preferred means. Alloys which contain these elements are specially heat-treated to form niobium carbides (Nb_2C). The C element then becomes no longer available to form Cr_{23}C_6 , leaving Cr free and available to provide corrosion resistance.

3. Metallurgical state and surface conditions

Many factors change the final properties of a dental

metal-ceramic alloy, such as the casting process, heating and cooling processes during casting, and the porcelain-fused-to-metal firing process¹¹. These processes may alter the metallurgical state, surface oxides, and corrosion properties of the alloy depending on its chemical composition. A multiphase (heterogeneous) alloy is more prone to corrosion than a monophasic or single-phase (homogeneous) alloy, due to a galvanic effect between areas of different compositions inside the alloy^{1,13}.

In light of these processes involved in alloy manufacturing, which may cause differences in the final properties among alloys, it is therefore important to use commercial alloy systems in research studies to facilitate comparison of results and finding among studies and if clinical relevance is desired. For these reasons, four commercial metal-ceramic alloys were selected for investigation in this study.

4. Local and systemic host environment

Ion release of dental alloys is also affected by environmental conditions, such as the acidity and composition of the surrounding electrolyte^{3,5,10,20,22,24,37}. An acidic environment (low pH) causes the electrochemical equilibrium to shift towards unfavorable conditions that lower generally the polarization resistance and increase the release of ions from alloys^{2,3,5,6,10,19-21,24,28,29,37}. The stability of Ni-based alloys has been shown to be significantly reduced when placed in more acidic environments, causing an increase in metal ion release⁵. Likewise, Co ion release from base metal alloys was significantly affected by low pH⁷. In a study by Strietzel and Viohl³⁰, it was concluded that when pH conditions became more acidic, the amount of ion release from non-precious and palladium alloys became higher (Figs. 1–2).

Can *et al.*³⁷ compared the ion release behaviors of a Ni-Cr alloy using artificial saliva (AS) and a cell culture medium. They reported that ion release was lower in the cell culture medium. In light of the ion release results obtained in previous researches which used cell culture media^{1,37}, AS and saline solutions were used in the present study instead of a cell culture medium. For Vrijhoef *et al.*³, a 0.9% saline solution (SS) of pH 5.3 was selected as the immersion medium to investigate the corrosion of ferromagnetic alloys used for magnetic retention of overdentures because it is an aggressive solution without inhibitory action. In the present study, the pH value of SS was adjusted to 7.3 so that it would not act as an aggressive solution. Instead, AS solutions with pH 2.3 (AS-LA) and pH 6.5 (AS-SS) were selected as the aggressive solutions to investigate the ion release of casting alloys. As shown in Figs. 1–4, ion release of all the tested dental casting alloys was found to be pH-dependent: markedly fewer ions were detected in SS (pH 7.3) than in AS-LA (pH 2.3) and AS-SS (pH 6.5).

Natural saliva is an extremely complex system with numerous constituents and variables according to the time of day. Thus, exact duplication is impossible³⁴. Covington *et al.*³⁸ studied the release of Ni and Be ions from base-metal dental casting alloys in artificial saliva

(AS) with different pH values. They found that decreased pH and increased immersion period up to 120 days resulted in enhanced Ni and Be release. In the present study, AS-LA with pH 2.3 was used to examine the corrosion behavior of alloys under the worst-case condition. Indeed, highest ion release results were obtained in AS-LA immersion for all metal-ceramic alloys. In particular, Pt ion release ranked the highest after 60 days of immersion in AS-LA solution. In the context of the present study, this caused PSR alloy to exhibit the highest ion release result among all the tested alloys. Nonetheless, 7-day ion release results of Au-Pt-based PSR alloy in AS-LA immersion (Table 5) were consistent with the results of an Au-Pt-based alloy (V-Gnathos Plus) of a previous study which concluded that its corrosion resistance was acceptable³².

In the present study, the presence of Cl ions in all the three immersion solutions rendered them as electrolytic media. Increase in Cl ion and decrease in pH increased the aggressiveness of the electrolyte^{36,39}. Cl ion from NaCl at pH 2.3 with H ion acted as HCl solution on Fe ion. Consequently, elemental Fe was released from the alloys into the immersion solutions as Fe ion (Figs. 1–3). Despite the low Fe content in the alloys, its extremely high affinity resulted in the release of a large quantity of Fe ion.

Proteins in immersion solutions have an effect on metallic corrosion, by virtue of the formation of metal-protein complexes on alloy surfaces²⁸. Mezger *et al.*²⁰ evaluated the effect of mucin (an organic compound) on the corrosion behavior of dental casting alloys at different pH levels. Mucin hardly exerted any influence at a low pH value; however, it seemed to act as a cathodic inhibitor at a high pH value. Based on this finding²⁰, mucin was omitted from AS solutions in this study as its presence in either AS-LA or AS-SS with low pH values would be inconsequential. Compared with immersion in SS alone, the presence of proteins in SS was found to enhance the release of Ag, Cu, Pd, and Zn ions — but the opposite was reported for Ni-Cr alloy. In a recent study by Bilhan *et al.*³³ which investigated the effect of salivary proteins (mucin, IgA, urea, and lysozyme) on the corrosion of dental amalgam, pure Ti, Co-Cr-Mo and Ni-Cr-Mo alloys, it was revealed that Ni-Cr-Mo and dental amalgam alloys were highly susceptible to corrosion whereas Co-Cr-Mo alloy and pure Ti exhibited passive behavior. Salivary proteins appeared to enhance passive film formation on Ti surface, thereby inhibiting corrosion. Although no salivary proteins were selected in the current study, the corrosion behaviors of pure Ti, Co-Cr-Mo and Ni-Cr-Mo alloys observed by Bilhan *et al.*³³ agreed with the present study.

Corrosion measurement methods

All dental cast alloys release metal ions — with varying amounts and of varied types — into the oral environment which have the potential to interact with oral tissues²⁸. Interestingly, the amounts of metal ions released do not reflect their relative weight contents in an alloy's composition²⁸. The conventional method to determine

corrosion rates is the weight loss method which requires long-term exposure. The primary advantage of this test method is that it resembles the real application. The main disadvantage is that it is difficult to keep the variables under control throughout the entire exposure period.

Alternatively, electrochemical methods can be used to characterize the corrosion properties of metals and metal alloys. In the present study, AAS was used to analyze ion release. Unlike calorimetric analysis and ultraviolet spectrophotometry, AAS can accurately and rapidly measure ion concentrations to levels below 1 ppm²⁶⁾. For a complete picture of the corrosion behavior of the four selected commercial dental alloys, a two-pronged strategy was used in this study: AAS determination of ion release at different pH values (Figs. 1–4) and SEM analysis of sample surfaces before and after immersion in different pH media (Figs. 5–8).

According to Wataha and Malcolm⁴⁰⁾, SEM analysis revealed no differences in the surface appearances of alloys up to $\times 1,000$ magnification before and after a 30-day exposure to a cell culture medium. In the present study, however, WBC and W99 samples immersed in AS-LA and AS-SS showed noticeable differences in SEM micrographs acquired at the same magnification (Figs. 5(b)–(c) and 6(b)–(c)).

Corrosion behavior of Ti

Compared with other non-noble dental alloys, pure Ti reportedly had better corrosion properties and biocompatibility^{14,24,30)}. In this study, RTI alloy showed moderate ion release in all the immersion solutions — which could be attributed to a passive oxide film covering the titanium alloy surface.

In a study by Cheng *et al.*¹⁶⁾, all the experimentally prepared Ti alloys showed excellent corrosion resistance without any breakdown in Hanks' solution at 37°C. Hanks' solution has a high concentration of Cl ions, and Ti and Ti alloys assume excellent corrosion resistance under the influence of Cl ions. In the present study, the largest amount of Ti was released from RTI in acidic AS-LA solution while no Ti was released when immersed in SS.

Taira *et al.*²¹⁾ studied the mechanical properties and corrosion resistance of various cast Ti alloys. They concluded that cast pure Ti had mechanical properties similar to those of type 4 (extra hard) Au alloy. As for cast Ti alloys, they were immune to corrosion attacks in the oral environment — even under highly acidic surroundings. The strong passivity trend exhibited by all the cast Ti alloys²¹⁾ agreed with the RTI alloy results of the present study.

Corrosion behavior of noble metals and alloys

High-Au alloys are highly corrosion-resistant^{14,29)}. They also exhibited the best clinical and *in vivo* results against tarnish^{29,39)}, and it was found that patient-related factors had as much influence on the corrosion resistance as the microstructure of the alloy. Wirz *et al.*²⁹⁾ conducted both *in vitro* and *in vivo* experiments to evaluate and compare

ion release from Au-based, Co-based, and Ni-based dental casting alloys. Findings of both *in vitro* and *in vivo* studies supported each other. The results of PSR, WBC, and W99 alloys in the present study were also consistent with their *in vitro* results²⁹⁾.

Using a cell culture medium as the immersion medium, Wataha *et al.*¹⁵⁾ reported absence of Au ion release from high-noble alloys. However, in the present study, Au ions were detected in all the three immersion media. Using AS as the immersion medium and with X-ray diffraction analysis, Brune *et al.*¹⁴⁾ detected considerable amounts of Au released from the Au alloys but Ti corrosion products could not be assessed in view of faint activity levels. In a recent study on ion release using experimental Au-Pt-based metal-ceramic alloys immersed in deionized water and a commercial soft drink¹⁰⁾, similar ion release results were reported for the corresponding pH levels.

In another study³²⁾ which evaluated the corrosion resistance of dental alloys using chemical and electrochemical corrosion tests, Au-Pt alloys were found to release a higher quantity of ions compared with other precious alloys, but lower than Ni-Cr alloys. Using both AS and SS as the immersion media and evaluation by means of microphotography and SEM, Johansson *et al.*³⁹⁾ reported that Cu-based and Be-containing Ni alloys showed more tarnish and corrosion than did Ni and Au alloys — findings similar to those of W99 and PSR alloys in this study (Figs. 6 and 8).

In the absence of detailed data on corrosion for an alloy, use of high-noble and noble alloys of single-phase microstructure will minimize biological risks because ion release from these alloys is lower. However, detailed ion release data are always preferred because even with similar compositions, each alloy exhibits somewhat different ion release behaviors⁹⁾.

CONCLUSIONS

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

1. Results of *in vitro* corrosion studies depend on instrumentation and experimental variables. Differences in study designs and chemical factors make comparisons between corrosion studies more difficult.
2. The *in vitro* corrosion behavior of WBC alloy was better than that of W99 alloy. Total ion release of W99 alloy after 60-day immersion in AS-LA solution was 9.92 wt%, approximately twice that of WBC alloy (5.26 wt%). Nevertheless, both alloys were considered as adequately corrosion-resistant.
3. The *in vitro* corrosion properties of W99 and WBC alloys were dependent on their chemical compositions. W99 contained 22.5% Cr and 9.5% Mo, and its high Cr and Mo content augmented its resistance to corrosion attacks.
4. Results of this *in vitro* corrosion study showed that the four selected commercial alloys were well

suiting for dental usage. As a rule of thumb, prudence dictates that dental practitioners should know the complete composition of each alloy used and use only alloys that show the lowest ion release rate.

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