The Release of Ions from the Base Co-Cr-Mo Casting Alloy *in vitro* into the Phosphate Buffer at pH 6.0

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Summary

The purpose of this study was to examine how WIRONIT® alloy behaves in phosphate buffer at pH 6.0 (which simulate human saliva) over a relatively long period of time and to establish the type and amount of ions released from the casting alloy. The study also attempted to determine the influence of the time period, during which the casting alloy was exposed to the phosphate buffer at pH 6.0. Sixty commercial samples of WIRONIT® alloy (8 mm in diameter and 15.8 height) were tested. Release of ions was measured on ten occasions: 1, 2, 3, 4, 5, 6, 7, 14, 21 and 30 days. An analysis of the solution into which samples of the tested alloy were plunged using inductively coupled plasma atomic emission spectrometer (ICP-AES) showed that cobalt (Co), chromium (Cr), iron (Fe), zinc (Zn) and nickel (Ni) ions were released during the month. Co ions were released from the base Co-Cr-Mo alloy in the greatest amount while Fe ions were released in the smallest amount. The results of this study indicate that the time of exposure to the phosphate buffer at pH 6.0 had statistically significant influence ($p<0.01$) in the release of all detected ions from the Co-Cr-Mo alloy.

Key words: *ion release, Co-Cr-Mo alloy.*

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Introduction

When selecting a dental casting alloy for fabrication of removable partial denture frameworks, three basic factors influence the clinician's decision: physical properties of the alloy, cost and biocompatibility (1).

Dental alloys are exposed daily to different conditions in the oral cavity which offer ideal conditions for corrosion and chemical degradation of most dental materials. The materials employed in the mouth must be completely tarnish-resistant, they must not react with the many alkaline and acid foods that are taken into the mouth, and they cannot be affected by mouth fluids. Furthermore, they must be extremely strong so that the small, delicate tooth restorations and appliances will not be broken or bent by the forces exerted during chewing (2).

As the price of gold significantly increased in the 1970s, alternative cheaper cobalt-chromium alloys came appeared on the dental market. Thanks to modern tehnology of casting and polishing dental alloys, cobalt-chromium alloys today are widely used in prosthetic dentistry for fabrication of removable partial dentures and also for fabrication of some fixed prosthetic appliances. Advantages of using these dental alloys for casting prosthetic appliances are their low weight and good mechanical properties, such as great hardness, strength, resistance to tarnish and high temperatures and also resistance to corrosion.

Cobalt-chromium alloys are solid alloys with about 64% cobalt and 29% chromium. Although cobalt and chromium are major components of these casting alloys and constitute more than 90% of their mass, other components such as molybdenum, carbon, manganese, iron, silicon, beryllium, tungsten, boron and titanium have a great influence on the mechanical and physical properties of these alloys (3).

The humid, warm oral cavity offers ideal conditions for corrosion of the metal surface and its dissolving. Foods and drinks are usually very acid or alkaline. Different organic acids, such as lactic and piruvic acid, are created after disintegration of food's rests (2). Organic acids decrease pH value inside the oral cavity and may have a negative effect on ione release from dental alloys.

Metal ions which are released from dental alloys in the oral cavity can lead to either toxic or allergic responses (4). Furthermore, they can be transferred to distant organs, thereby causing different changes (5).

Many recent studies examined ion release from dental alloys in different conditions. They showed that the alternative alloys, which appeared on the market as a result of the high price of gold, release much more ions than the conventional alloys with a high share of gold (6, 7). They also proved that ion release from different dental alloys wasnot directly proportional to ion concentration in the alloy. Some elements are much more unstable than others and this phenomenon is known as "selective dissolving" (8).

The purpose of this study was to examine how the Co-Cr-Mo alloy WIRONIT® behaves in a phosphate buffer at pH 6.0 over a relatively long period of time and to establish the type and amount of ions released from the alloy. Likewise, the aim of this study was to establish the influence on ion release of the time period, during which the alloy was exposed to the solution.

Materials and methods

Cobalt-chromium-molybdenum alloy WIRONIT®, manufactory characteristic BS 3366 Part I, 1988, was examined. The alloy is a product of BEGO manufacturers (Germany), and in its composition the main component is cobalt (Co) with 64% share.

Commercial samples of Co-Cr-Mo alloy which were originally fabricated by the manufacturer as rollers were tested. All the samples had the same dimensions: 8 mm in diameter and 15.8 mm in height.

To eliminate superficial impurity the samples were disinfected with alcohol and then thoroughly washed twice with sterile water. Subsequently the samples were dried with sterile gauze.

The phosphate buffer at pH 6.0, which was composed according to the established pharmacopeial standards, mimicked human saliva. The ion release from the alloy was measured on ten occasions: after 1, 2, 3, 4, 5, 6, 7, 14, 21 and 30 days. Six samples were used for each time period (n = 6), i.e. a total of 60 samples were tested.

After thorough cleaning and drying the samples were secured in 15 mL sterile test tubes of very fine glass. 10 mL of phosphate buffer was added to the test tubes which were then sealed with plastic seals. The test tubes were marked and placed into a thermostat at 37°C to mimic the temperature of the oral cavity environment.

After beeing submerged in the given solution over a period of 1, 2, 3, 4, 5, 6, 7, 14, 21 and 30 days respectively, the samples were taken out of the test tubes. To obtain data on the type and amount of ions released from the tested alloy the solutions were analysed by means of inductively coupled plasma atomic emission spectrophotometry (ICP-AES; JY 50 P, Jobin Yvon, France). This device ensures the quality and quantity analysis of the elements released in the argon plasma by means of high frequency in amounts larger than 10 μg/L. Atoms of different elements, released from the tested samples, are excited by the argon plasma. By returning these atoms to lower energetic levels, light of different wavelengths is generated. The light is typical for each element (quality analysis). Intensity of the light is directly proportional to the amount of the appropriate element in the sample (quantity analysis) (9).

SPSS for Windows was used for statistical analysis and data presentation (descriptive statistics, one-way variance analysis, Sheffe's post-hoc tests, Friedman's nonparametric test).

Results

Solutions in which the Co-Cr-Mo alloy samples were submerged were analysed by means of ICP--AES (Table 2, Figure 1). Five types of metal ions were released in the phosphate buffer at pH 6,0 over one month: cobalt (Co), chromium (Cr), iron (Fe), zinc (Zn) and nickel (Ni).

The results indicate that the greatest amount of Co ions were released into the phosphate buffer at pH 6.0 from day one. Other metal ions were released in considerably smaller amounts when compared to Co ions, although a constant increase in release of all ions was observed by the end of exposure to the phosphate buffer at pH 6.0.

The results of analysis of variance are shown in Table 3. There was significant difference ($p < 0.01$) in ion release, depending on the different time of exposure of the Co-Cr-Mo casting alloy to the phosphate buffer at pH 6.0.

Whereas analysis of variance showed statistically significant difference in ion release, depending on the different time of exposure of the tested alloy to the phosphate buffer, Sheffe's post-hoc tests were made for each ion. It was found that release of cobalt (Co) and chromium (Cr) ions in the first five days was significantly different than during the 6th, 7th, 14th, 21st and 30th day. Release of iron (Fe) ions during the first six days of exposure was significantly different from Fe ion release on the 7th, 21st and 30th day. Release of zinc (Zn) ions during the first four days of measurement was significantly different from Zn ion release on the 5th, 6th, 7th, 14th, 21st and 30th day. Nickel (Ni) ion release was significantly higher on the 21st and the 30th day of exposure compared with all other days.

Friedman's nonparametric test for several dependent variables was used to compare the amount of release of different metal ions (Table 4). The analysis demonstrated that significant difference existed between the quantity of different metal ion released throughout out the period of observation ($p < 0.001$). The highest amounts of Co, Zn, Ni and Cr ions were released at the end of the measurement, and Fe ions were released in the smallest amounts.

Discussion

Five types of metal ions were released from the samples of Co-Cr-Mo alloy (WIRONIT®, BEGO, Germany) examined in this study: cobalt (Co), chromium (Cr), iron (Fe), nickel (Ni) and zinc (Zn). Although the manufacturer didnot state the presence of iron, zinc and nickel, significant amounts of these ions were recorded, especially Zn ions, at the end of exposure.

Some studies which examined ion release from different alloys over several months, showed that the amount of the released ions was high at the beginning of the examination. After the proper time, balance was established with linear ion release in relation to time (10).

The results of this study reveal that ion release from the tested alloy depended on the time of exposure to the phosphate buffer at pH 6.0. Concentrations of all recorded ions increased slowly during the time of exposure. This data is very important because Co-Cr-Mo alloy, as the material of choice for fabrication of partial denture framework, is placed in the patient's mouth for a long time.

Normally Co, Cr, Fe, Ni and Zn are present in small concentrations in the human body as trace elements. Although sufficiently small concentrations of these ions were recorded in this study, for some elements (Ni and Cr) they exceeded normal daily dietary intake (11, 12). Although Ni is thought to be an essential micronutrient, intercellularly it is capable of binding to and depolymerizing RNA and proteins, as well as disrupting muscle contractibility and enzyme function (13).

Ion release from dental alloys is unavoidable and is hard to find an alloy which will be entirely stable in the human body and will not show signs of biodegradation. Examining ion release from eight different dental casting alloys (noble and base metal alloys) over a 10-month period, Wataha and Lockwood (10) concluded that different elements have different tendencies to be released from an alloy. Nelson et al (1) determined that conditioning of casting alloys with biologic solutions accelerates elemental release by removing initial labile elements. The authors consider that conditioniong of dental casting alloys before delivery to the patient could decrease the exposure of oral tissues to labile elements.

Low concentrations of metal ions can cause different changes of oral tissue cells which are in direct contact with an alloy. It has been demonstrated that nickel, which is released from dental casting alloys, deposits in cells over extended periods of time, thus having adverse effects on living cells when deposited in higher concentrations (14). Jacobsen (15) found that low concentrations of nickel, approximately 2.5 mg/mL, had adverse effects on human gingival cells in a tissue medium culture. In sensitive patients even small amounts of Ni ions can produce allergic responses. Apart from local allergic alterations on the oral mucosa some cases have also been reported of systemic skin reactions (16, 17). Patch testing has been carried out on a great number of patients, subsequently resulting in positive reactions to some components of dental alloys, particularly to those containing nickel and chromium (18). The results of most recent epidemiological studies indicate that cobalt, chromium and nickel, which are released from dental alloys, are metals which most often produce allergic responses (19).

95% interval of confidence for ion release from the tested alloy (Table 2) showed that there was significant variation in Ni and Co ion release. Whereas in this study commercial samples of Co-Cr-Mo alloy of equal chemical composition were used, it can be presumed that superficial damage of individual samples or irregularity inside the crystalline structure of the metal caused variation in ion release. These irregularities which arose during the manufacture of the alloy thus lead to reduction in stability of some elements.

Before beeing placed in the patient's mouth, dental casting alloy must go through several technological procedures, such as melting, casting, cooling and polishing. During these procedures some irregularities inside the alloy's crystalline structure may occur. Based on data of this study it can be presumed that there will be an even greater increase in the rate of the released ions in subsequent development of events when alloy is processed in the laboratory.

Conclusions

1. Cobalt (Co), chromium (Cr), iron (Fe), zinc (Zn) and nickel (Ni) ions were released from commercial samples of WIRONIT® alloy into the phosphate buffer at pH 6.0 during one month.
2. Although the manufacturer didnot state the presence of zinc, iron and nickel in the declaration for WIRONIT® alloy, significant amounts of these ions were released from the tested samples.
3. Release of cobalt, chromium, iron, nickel and zinc ions from the tested alloy depend on time of exposure to the phosphate buffer at pH 6.0.
4. The greatest amount of cobalt (Co) ions were released from the samples of Co-Cr-Mo alloy during exposure to the phosphate buffer at pH 6.0, while iron (Fe) ions were released in the smallest amount.