

# The Release of Nickel Ions from Three Different Dental Casting Alloys

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## Summary

*The objective of the current study was to investigate the release of Ni ions from the following three dental casting alloys: high-noble Au-Pt alloy, and non-noble (base metal) Ni-Cr and Co-Cr-Mo alloys. The purpose of the study was also to determine whether the solution in which an alloy is submerged as well as its pH level and the exposure time have any effect on the amount of released Ni ions from the three above mentioned alloys.*

*Three commercial alloys were used in the experiments: two base metal alloys, Ni-Cr (Wiron 99<sup>®</sup>, Bego, Germany) and Co-Cr-Mo alloy (Wironit<sup>®</sup>, Bego, Germany) and one high noble, Au-Pt alloy (Noble Metals Refinery, Zagreb, Croatia). Ni-Cr alloy samples and Co-Cr-Mo alloy samples, rollers of identical dimensions with diameters of 8 mm and heights of 15.8 mm were used, made by the manufacturer. The samples of Au-Pt alloy were plates with dimensions of 8 mm and height of 1 mm, also made by the manufacturer.*

*All the samples were submerged in three different solutions over a certain period of time. The phosphate buffered solution at the pH = 6 level, represented human saliva, whereas lactic acid, to which certain amounts of acetic and formic acids, pH=3.5 (0.1 M lactic acid, 0.1 M NaCl, 1% acetic acid and 1% formic acid) were added to represent the condition that is created below dentobacterial plaque.*

*The phosphate buffered solution (pH=3.5), which was composed according to established pharmacopeical standards was used for comparison, since such extremely acid conditions do not exist in the oral cavity environment.*

*Six samples were used for each tested dental alloy (n=6), for each solution separately and for each tested time interval, and thus 180 samples were used or 540 samples in total.*

*The ion release from the above tested dental alloys in the above mentioned solutions was measured over 10 time intervals, i.e. after 1, 2, 3, 4, 5, 6, 7, 14, 21 days and 30 days respectively.*

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Solutions were analysed by atomic absorption spectrometar with inductively coupled plasma (ICP - AES) JY 50, France.

Results of the analysis lead to the following conclusions:

1. In the following dental alloys (Ni-Cr, Au-Pt, Co-Cr-Mo) the manufacturer states the presence of Ni only in Ni-Cr alloy. Results show that Ni-Cr alloy and Co-Cr-Mo alloy released Ni ions, but the Au-Pt alloy did not, even at low pH levels.
2. During the initial period of exposure Ni ions were released from the Co-Cr-Mo alloy in small amounts (10 µg/L) while increase in ion release was observed on the sixth day in the phosphate buffered saline at pH 3.5. Significant Ni ions release also occurred on the 21<sup>st</sup> day and 30<sup>th</sup> days respectively in the phosphate buffered solution at pH 6 (artificial saliva) as well as in lactic acid at pH 3.5 (dentobacterial plaque) when amount of the Ni ion release exceeded the approved daily dietary intake of this oligo-element.
3. The Ni-Cr alloy released great amounts of Ni ions in all three solutions so that on the very first day of measurement these amounts exceeded the approved daily dietary intake of this element. Gradually, the amount of the released Ni ions increased with great variability in all solutions. However, the greatest increase in Ni ions release was noted in the phosphate buffered saline, at pH 6 level (artificial saliva) where it exceeded the approved daily dietary intake of this element. Therefore, this alloy should be used exclusively for fabrication of metal-ceramic appliances and should be fully covered by ceramic.

Key words: release, nickel, dental alloys.

## Introduction

Dental casting alloy should not be toxic. They should also be resistant to corrosion, which means that they should not chemically react with either acids or alkaline solutions. In addition, they should have good physical and technological properties such as hardness and strength. Besides, which they should be suitable for heat processing. Furthermore, such alloys should be available for patients at low cost. Since the price of gold rose dramatically in the 1930s, a large number of new, non-noble alloys were developed for use in dentistry apart from the Au-Pt alloy. The Au-Pt alloy is a high noble alloy, while the Co-Cr-Mo alloy used for fabrication of casting alloy (metal framework) dentures or the Ni-Cr alloy used for dental metal ceramic appliances are base metals or non-noble alloys (3).

All the alloys available on the dental market should undergo the following three stages of testing: *in vitro* testing on laboratory animals, *in vivo* testing on laboratory animals and *in vivo* testing on patients. According to the specification of the American Dental Association the most important feature which should be tested before the alloys are available on the dental market is their biological feature, that is their biocompatibility (4).

When a prosthetic appliance is inserted into the oral cavity dental alloy, it is in contact with saliva. Saliva is a hypotonic solution (K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>++</sup>, Mg<sup>++</sup>, inorganic phosphates, bicarbonates, serum proteins: IgG, IgM, IgA, albumins, salivary enzymes, mucoproteins, glycoproteins, hormones, carbohydrates, lipids, nitrogen compounds, lactoferin) (5). It is also a good conductor of electricity, so that electrochemical corrosion occurs, particularly when

two or more different alloys are present in the oral cavity (6). There is a large number of alloys that meet the requirements regarding their mechanical, physical and technological properties. Yet, very often, such alloys are not resistant to corrosion (7). Metal ions which are released from dental alloys in the humid oral cavity medium can lead to either toxic or allergic responses. Furthermore, they can be transferred to distant organs, thereby causing different changes (9).

Base metal alloys exhibit a greater number of released ions than the alloys containing larger amounts of gold (10, 11). Schmaltz ranked elements according to their cytotoxicity as follows: Ag, Zn, Cd, Hg, Pt, Cu, Ni, Pd, Mn, Nb, Mo, Ga, Cr, In, Sn (12).

A study of 16 different metal alloys was carried out to measure their cytotoxicity according to the amount of the released ions. Using different procedures and methods the researchers demonstrated that the alloys of more complex composition were more toxic than those of less complex composition (13).

Craig and Hanks (14) reported a reduction of cytotoxicity in Ni-Cr alloys containing 16-27% of Cr which occurred due to the presence of Cr (III) oxide overlay. They also noted that this overlay prevented the ions from further release in large amounts. In addition, it was found that when a cell culture of human fibroblasts was attached to the Ni-Cr-Mo alloy it appeared to decrease type III collagen production. Bumgardner et al. further determined that the Ni ions which were released from the Ni-Cr alloy had an adverse effect on cell proliferation. When the cells were grown in different culture media, a different effect were observed. Ni applied to a tissue culture medium exhibited greater cytotoxicity than Cr (15).

The ions released from an alloy may cause allergic responses that can be either local or systemic (16). Using the patch test Dooms-Goossens et al. (17) noted that in most cases patients had positive responses to Cr, and particularly to Ni. Allenby and Goodwin (18) determined that the rate of 112 ppm of Ni (<0.05% nikel-sulfat) was needed to obtain a positive response. Franz found that Ni, Cr and Co (19) are the most common allergens. Peltonen noted that women are ten times more sensitive to Ni compared with men (20). Freeman et al. determined that the effect of Ni depends on the chemical form in which Ni is exhibited in the body. Thus (Ni (CO<sub>4</sub>)),

(NiS) and (Ni<sub>3</sub>S<sub>2</sub>) exhibited the strongest carcinogenic effect. Ni is considered to be the most common allergen in dental alloys (22, 23), however some dental alloys release Ni ions in amounts that are almost identical to those prescribed as a daily dietary intake of this element. On the other hand, the amounts of Au, Pd, Ag, Cu and Zn are considerably below the dose of these oligoelements, considered to be appropriate in a daily dietary intake (24).

The ion release from an alloy does not necessarily correlate to the abundance of this element in the alloy. Rather, there is a selective dissolution so that the elements that are present in alloys only in traces can release from them in larger amounts (25). Wataha determined that, unlike high-noble alloys, less noble alloys continue Ni ion release for several days after their exposure to an acid medium (26). Covington et al. (27) found that Ni was released from the less noble alloys (approximately 2.5 µg/cm<sup>2</sup>) over a 120 day period at as small pH level as 6. On the other hand, Geis-Gerstorfer and Pässler (28) proved that a large amount of the Ni ions was released from the Ni-Cr-Mo alloy (3300 µ/cm<sup>2</sup>) at 2.3 pH level over 35 days, which indicates the fact that both the less noble alloys and non-noble alloys are sensitive when exposed to an acid environment.

## Objective

Since Ni is one of a group of elements which improve the soldering ability of dental alloys it is commonly added to them, at least in minimal amounts. However very often the manufacturer does not state its presence. In addition, Ni is considered to be the greatest allergen. Moreover, Ni is cytotoxic and carcinogenic. The objective of this study was to investigate how different factors such as the solution type in which the alloy is submerged, the pH level and exposure time affect the amount of released Ni ions from the three above mentioned alloys.

## Materials and Methods

The release of Ni ions from dental casting alloys was measured. The alloys were as follows: two non-noble alloys, Ni-Cr alloy and Co-Cr.Mo alloy, and one high-noble alloy, Au.Pt alloy. The tested Ni-Cr

alloy was Wiron 99<sup>®</sup> custom fabricated by BEGO, Germany. According to the manufacturer's declaration the alloy contained the following elements: Ni-65%, Cr-22.5%, Mo-9.5%, Si-1%, Nb-1%, Ce-0.5%, Fe-0.5% and C<0.02%. The tested Co-Cr alloy was WIRONIT<sup>®</sup> custom fabricated by BEGO, Germany. The alloy contained the following elements: Co-64%, Cr-28.65%, Mo-5%, Si-1%, Mn-1%, C-0.5%. The Au-Pt alloy was manufactured by the Noble Metals Refinery, Zagreb, Croatia. According to the manufacturer's declaration the alloy contained the following elements: Au-75%, Pt-8%, Ag-9.5%, Cu-5.1%, brass (the Cu-Zn alloy) 1.5% and some other elements 0.9%, respectively.

The samples of Co-Cr-Mo and Cr-Ni alloy were originally fabricated by the manufacturer as rollers of dimensions 8 mm in diameter and 15.8 mm in height. The samples of Au-Pt alloy were originally fabricated by the manufacturer in platelets with dimensions as follows: 8 mm x 6.5 mm x 1 mm.

All the samples were submerged in three different solutions over previously determined time intervals. The phosphate buffered saline (pH=6), which was composed according to established pharmacopeial standards, represented human saliva, while lactic acid to which certain amounts of another two acids were added (lactic acid 0,1 M; 0,1 M NaCl, acetic acid 1% and formic acid 1%) represented *in vivo* conditions below dentobacterial plaque.

The phosphate buffered solution of pH 3.5 (composed according to pharmacopeial standards) was used to ensure comparison, since such acid conditions do not exist in the oral cavity environment.

Ion release from the alloys was measured over the following time intervals: on the 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup>, 4<sup>th</sup>, 5<sup>th</sup>, 6<sup>th</sup>, 7<sup>th</sup>, 14<sup>th</sup>, 21<sup>st</sup> and 30<sup>th</sup> day, respectively. Six samples were used for each alloy (n=6). The same number of samples was used for the solution as well as for the time interval thus making 180 samples of each tested alloy. Thus, the total number of tested samples was 540.

Prior to rinsing with alcohol each sample was thoroughly cleaned by scrubbing with a soft toothbrush. Subsequently the samples were dried with sterile gauze and then secured into 15 ml sterile glass test tubes. The tubes were sealed with plastic seals. 10 ml of lactic acid (plus 1% of formic acid and 1% of acetic acid) (pH=3.5) was added to the

first 180 tubes by means of a pipette. An identical amount of phosphate buffered saline was added to the next 180 test tubes (pH=6). Then 10 ml of phosphate buffered saline (the pH=3.5) was added to the remaining 180 test tubes. The test tubes were labelled. The clean samples were submerged into them. The test tubes were then placed into a thermostat at 37°C to simulate the temperature of the oral cavity environment. Having been submerged in the given solution for 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 alloys the solutions were analysed by means of atomic spectrophotometry. The spectrophotometers used with inductively coupled plasma (ICP-AES), JY 50 P, France, is located in the Institute for Research in Geology, Zagreb, Croatia. This device ensures two analyses: quality analysis and quantity analysis of the elements released in argon plasma by means of high frequency energy. Simultaneously a temperature of approximately 8000 K develops. Light of different wavelengths generated within the source of the inducing coupling plasma is directed by means of a focal lens towards an optical unit on the device which is called a polychromator. The device for atomic absorption spectrophotometry consists of a quality spectrometer for the ultraviolet and visible area with a bar. It also consists of a photomultiplier which is a detector. This device picks up the created radiation and transforms it into electric signals which are further transmitted into the processing unit (IBM-32 byte computer) The link between the two devices (the JY 50 P and the IBM computer) is controlled by a microprocessor SPECTRALINK (29). The electronic equipment of the device ensured measurement of concentrations of each element in one of five ranges of potencies (for example either from 1 µg/L to 0.1 µg/L or between 1 mg/L and 100 g/L). SPSS for Windows was used for statistical analysis and data presentation (descriptive statistics, variance analysis).

## Results and discussion

Nickel ions were released from the Ni-Cr alloy as well as from the Co-Cr-Mo alloy. However, they were not released from the Au-Pt alloy. Although the manufacturer did not state the presence of nickel

in the Co-Cr-Mo alloy Ni ions were released from it. The amount of released Ni- ions from the Ni-Cr alloy and from the Cr-Co-Mo alloy in the three tested solutions over a period of 1, 2, 3, 4, 5, 6, 7, 14, 21 and 30 days respectively, and standard deviations are shown in Table 1.

It was apparent that there were differences in the amounts of the released Ni- ions from the alloys. Thus the Ni-Cr alloy released a significantly greater amount of Ni-ions in all the solutions when compared to the Co-Cr-Mo alloy (Table 1, Graph 1, Graph 2). Also, the difference between the two alloys was statistically significant ( $p < 0,01$ , Table 2).

During the period of the first five days Ni-ions were released from the Co-Cr-Mo alloy in the three tested solutions in small amounts, so that their presence was hardly detectable by the device ( $10 \mu\text{g/L}$ ). An increase in the number of the released ions was recorded on the sixth day in the phosphate buffered saline pH 3.5, in which the ion release reached the greatest rates on the 30th day. However, the above described conditions do not exist in the oral cavity.

In the phosphate buffered saline of pH 3.5 (artificial saliva), an increase in ion release was also documented on the 21<sup>st</sup> and 30<sup>th</sup> day, respectively. However, the rates of the ion release did not exceed the value of  $200 \mu\text{g/L}$ .

The same increase in ion release occurred in the lactic acid medium, the pH 3.5, which, in this experiment, represented the acid environment that can be found in humans either below deposits of dentobacterial plaque on the teeth or on the surface of prosthetic appliances. In both cases, dentobacterial plaque is formed as a result of inadequate personal oral hygiene.

The daily dietary intake of nickel in women should be approximately  $90 \mu\text{g}$ , compared to men who need to take  $97 \mu\text{g}$  of this element per day (30). In this experiment the rate of the released Ni-ions exceeded the approved daily dietary intake of nickel.

Exposure time, as well as a combination of exposure time and solution type, had a statistically significant effect on the Ni-ion release ( $p < 0.05$ , Table 2).

A considerable release of the Ni-ions from the Ni-Cr alloy was also documented in the experiment. The amount of the released Ni-ions exceeded the

approved daily dietary intake of nickel as early as the first day of exposure. Subsequently, a constant increase of Ni-ions release from the Ni-Cr alloy was documented on the following days (Table 1, Graph 1, Graph 2). It reached a climax on the 21<sup>st</sup> day with the highest rate of more than  $1000 \mu\text{g/L}$  in the phosphate buffered saline, pH=6. The Ni-ion release in lactic acid reached the highest rate on the 14<sup>th</sup> day when it was over  $1000 \mu\text{g/L}$ .

Extremely great deviation from mean values (great variability) was determined in Ni-ion release from the Ni-Cr alloy (Table 1), so that the amount of released Ni-ions from one sample in the phosphate buffered saline, pH=6, almost exceeded the approved dose by reaching a rate as high as  $2739 \mu\text{g/L}$ . This variability of Ni-ion release from the Ni-Cr alloy indicates deviations from the generally adopted quality standards that have been established for alloys. It is apparent that some manufacturers do not follow the rules regarding the production of quality alloys. Moreover, based on the data we can hypothesise that there will be even greater increases in the rate of the released ions in subsequent developments of events when alloys are processed in the laboratory (melting, casting, cooling, polishing).

In 1993 Geis-Gerstorfer and Pässler (28) measured Ni-ion release from some alloys. They documented even greater rates of Ni-ion release from Ni-Cr alloy. Unlike the samples in our experiments their samples were submerged in a solution which had a smaller pH value (pH=2.3).

In this study the type of solution and the pH value did not have any significant effect on Ni ion release, even in cases when combined with the exposure time, although the greatest amount of Ni ions released was observed in later intervals and in phosphate buffered saline at pH 6 ( $p > 0.05$ , Table 3, Table 1).

It is known that allergic responses do not occur before the deposits of nickel in the human body have been filled (31).

The results of the current study reveal that the amount of Ni-ions released from the Co-Cr-Mo alloy increased with time. It was significantly greater in later intervals than during the first week of exposure, so that on the 21<sup>st</sup> day and on the 31<sup>st</sup> day the concentrations of Ni, in either the phosphate

buffered saline pH 6, or in the lactic acid pH 3.5, significantly exceeded the dose, that is considered to satisfy daily human need for this element. On the other hand, the Ni-ions released from the Ni-Cr alloy exceeded the daily dietary intake of Ni as early as the first day. Furthermore, some samples released as much as 20 times greater amounts of Ni-ions compared to the approved amount of daily dietary intake of nickel. Although nickel belongs to the group of essential micronutrients, it was established that it caused depolarisation of the RNA within the cell. In addition, it causes depolarisation of some proteins within the cell. Furthermore, Ni was found to have adverse effects on muscle contractability as well as on the function of some enzymes (32).

Wataha et al. demonstrated that there was a significant difference between the ion release rate from noble alloys and Ni based alloys. This difference was apparent after 30 minutes while the alloys were exposed to solutions of low pH values (26). According to Wataha, ion release from noble alloys did not significantly increase after the alloys had been exposed to solutions at low pH levels whereas the ion release from the semi-precious and non-precious alloys increased significantly with the decrease of the pH levels of the solutions in which the alloys had previously been submerged.

In this experiment ion release from the Au-Pt alloy was not recorded even in the solutions with extremely low pH levels, which could lead to the following two conclusions: 1-Ni was not present in the tested alloy or 2-Ni was not released from the tested alloy.

The manufacturer did not state the presence of nickel in the Co-Cr-Mo alloy. Nevertheless, quite significant amounts of Ni-ions were released from the Co-Cr-Mo alloy in all three solutions. This amount was particularly great at the end of the measurement (on the 21<sup>st</sup> and 31<sup>st</sup> day respectively).

It is unlikely that the low concentrations of Ni-ions, released from the Co-Cr-Mo alloy, would have any adverse effects either on distant organs or tissues of the human body.

The Ni-ion amount released from Ni-Cr in this experiment was much more than the approved daily dietary intake of nickel. Moreover, in some samples the amount of Ni ions released occasionally reached

a rate which was considered to exceed the approved daily dietary intake of nickel.

It has been demonstrated that nickel, which is released from dental alloys, deposits in cells over extended periods of time, thus having adverse effects on living cells when deposited in higher concentrations (33). Jacobsen found that low concentrations of nickel, approximately 2.5 mg/ml, have adverse effects on human gingival cells in a tissue medium culture (34). In sensitive patients even small amounts of Ni-ions can produce allergic responses. Apart from local allergic alterations on the oral mucosa there have also been reports of cases of systemic skin reactions (16). 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 (17). The results of most recent epidemiological studies indicate that cobalt, chromium and nickel, released from dental alloys, are the metals which most often produce allergic responses (19). Considering the fact that even extremely small amounts of a substance can produce an allergic response in a hypersensitive individual, we may conclude that certain amounts of the ions released from any prosthetic appliance is enough to produce such a response.

Allenby and Goodwin found that a level of Nickel concentration of 112 ppm (<0.05% nickel sulfate) was high enough to lead to a positive reaction when Ni patch testing was performed (18).

From the literature review it is apparent that Ni ions have adverse effects, both local and systemic. Therefore, precaution should be taken in cases when Co-Cr-Mo alloys, which released Ni ions on the 21<sup>st</sup> and 30<sup>th</sup> days at concentration levels higher than the approved doses of this element that are recommended as a daily dietary intake, are applied.

The amounts of Ni ions released from Ni-Cr alloy exceeded the amounts of Ni ions necessary in the daily dietary intake as early as the 1<sup>st</sup> day in conditions simulating saliva. Therefore Ni-Cr alloy should be used exclusively for metal ceramic appliances. The Ni-Cr alloy should not be used for fabrication of veneer crowns and telescopic systems in combined appliances, which is unfortunately the case today in clinical practice, due to the low cost of this alloy.

The use of Ni-Cr alloy should be indicated exclusively for ceramic appliances, since the entire surface of the alloy is overlaid with ceramics thus preventing direct contact with saliva in the oral cavity environment. Ceramics should even spread over the gingival margin of the crown, thus preventing the gingival margin from direct contact with both the saliva and acids which are found in dentobacterial plaque which is formed due to inadequate oral hygiene.

### Conclusions

1. In three dental alloys (Ni-Cr, Au-Pt and Co-Cr-Mo) the manufacturer stated the presence of Ni in only the Ni-Cr alloy. The results of the current investigation indicate that the two alloys, Ni-Cr and Co-Cr-Mo, released Ni ions, whereas the Au-Pt alloy did not even in cases of low pH levels.
2. During the first days of exposure Ni ions were released from the Co-Cr-Mo alloy in small amounts (10 µg/l), while an increase in release was observed on the 6<sup>th</sup> day in the phosphate buffered saline, pH 6 (saliva), as well as in lactic acid at pH 3.5 (dentobacterial plaque). It was also noted that the ion release exceeded the approved daily dietary intake of this oligoelement on the 21<sup>st</sup> and 30<sup>th</sup> day.
3. Great amounts of Ni ions were released from the Ni-Cr alloy in all three solutions as early as the first day of the measurement. This exceeded the approved daily dietary intake of nickel. The amount of the released Ni ions increased gradually with great variability in all solutions. However, the greatest variability rate was observed in the phosphate buffered saline of pH 6 (saliva) where it even exceeded the approved daily dietary intake of nickel. Therefore, Ni-Cr alloy should be used exclusively for fabrication of metal-ceramic appliances and should not be used for fabrication of veneer and telescopic crowns.