Coll. Antropol. **27** Suppl. 2 (2003) 99–106
UDC 616-74:615.465:616.314-089.27
Original scientific paper

Corrosion Behaviour of the Co-Cr-Mo Dental Alloy in Solutions of Different Composition and Different pH Values

Nives Rinčić[1], Ivo Baučić[2], Slobodan Miko[3], Milan Papić[4] and Esad Prohić[5]

[1] Public Health Center »Centar«, Zagreb, Croatia
[2] Department of Prosthodontics, School of Dental Medicine, University of Zagreb, Zagreb, Croatia
[3] Institute of Geology, Zagreb, Croatia
[4] Faculty of Practical Sciences, Split, Croatia
[5] Faculty of Science, Zagreb, Croatia

A B S T R A C T

The purpose of this study was to examine how Co-Cr-Mo dental alloy behaves in the solutions of different pH value and different composition over a relatively long period of time. Co-Cr-Mo dental alloy was exposed in vitro to either simulated saliva (phosphate buffer pH 6.0), a highly acidic medium resembling the extreme conditions in the oral cavity (phosphate buffer pH 3.5), and in lactic acid at pH which occurs under the dental plaque (lactic acid pH 3.5). The alloy samples were immersed in these three solution for 1, 2, 3, 4, 5, 6, 7, 14, 21, and 30 days. Solutions were analysed with the ICP-AES. The analysis showed that during one month cobalt (Co), chromium (Cr), iron (Fe), zinc (Zn) and nickel (Ni) ions had been released from tested samples in all three solutions. The results of this study indicate that the leaching of the Co, Cr, Fe, Zn and Ni ions in the solution was dependent both upon the nature of the solution in wich the alloy was immersed and the duration of the immersion (p<0.001).

Key words: *pH value, corrosion of Co-Cr-Mo alloy, time of exposure*

Introduction

Dental alloys are in direct contact with oral tissues and because of that they must be completely biocompatible: biologically tolerant (without causing antigen-antibody reaction), biochemically indifferent (remains unchanged in the body without causing any effect on the organism), electrically and magnetically inert

Received for publication April 28, 2003

(without causing a galvanic current or magnetic field)[1].

As the price of gold significantly increased in the 1970s, alternative cheaper cobalt-chromium alloys came to dental market[2]. Thanks to modern tehnology of casting and polishing dental alloys, cobalt-chromium alloys today are widely used in prosthetic dentistry for the fabrication of removable partial dentures and also for the 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 high hardness, strength, resistance to tarnish and high temperature and also resistance to corrosion.

Many dental casting alloys which have good mechanical properties, on the other hand aren't good enough from the aspect of corrosion because of their complex structure[2]. 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 must not be affected by mouth fluids[3]. Organic acids, which are created after disintegration of food remains decrease pH value inside the oral cavity and may have a negative effect on ione release from dental alloys.

Many recent studies 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[4,5]. Metal ions which are released from dental alloys in the oral cavity can lead to either toxic or allergic responses[6]. Furthermore, they can be transferred to distant organs, thereby causing different changes[7].

The purpose of this research was to examine how Co-Cr-Mo alloy behaves in the phosphate buffer at pH 6.0 and pH 3.5 and in the lactic acid at pH 3.5 as wellas to establish the type and amount of ions released from the alloy. Another aim of this study was to establish the influence on ion release of the nature of the solution and of the time period during which the alloy was exposed to the solution.

Materials and Methods

Commercial samples of Co-Cr-Mo alloy (WIRONIT^R, BEGO, Germany) which came as standard rollers (8.0 mm in diameter and 15.8 mm in height) were tested. The declared metal composition of the alloy is shown in Table 1. In order 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, was used as the lowest pH of freshly collected saliva. The phosphate buffer at pH 3.5, also composed according to the established pharmacopeial standards, was used to test the resistance of alloy to reduced pH values under extreme conditions. Lactic acid at pH 3.5, which came as a mixture of 0.1 M lactic acid and 0.1 M sodium chloride with 0.1% acetic acid and 1% formiatic acid, was used to represent the lowest end of pH under active plaque in oral cavity (formiatic and acetic acid are added in small quantities because of bacterial metabolism in dental plaque).

Six samples of Co-Cr-Mo alloy (n = 6) were immersed in every solution for either 1, 2, 3, 4, 5, 6, 7, 14, 21 or 30 days, i.e. a total of 180 samples were tested. The samples were secured in 15 mL sterile test tubes of very fine glass. 10 mL of each solution 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.

The type and amount of metal leached into the solution was assessed with the inductively coupled plasma atomic emission spectrophotomer (ICP-AES; JY 50 P, Jobin Yvon, France). The electronic equipment of the device ensured the measurements 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. The overall difference between the solutions and exposure time was assessed by means of ANOVA.

Results and Discussion

Five types of metal ions were released from the samples of Co-Cr-Mo alloy which was examined in this research: cobalt (Co), chromium (Cr), iron (Fe), nickel (Ni) and zinc (Zn). The presence of these ions was recorded in all solutions (phosphate buffer pH 3.5, phosphate buffer pH 6.0 and lactic acid pH 3.5). Most of the principal declared metal constituents of the Co-Cr-Mo dental alloy did not leach into these solutions, whereas some of the undeclared metals did leach in the amounts well above their detection limit. Thus, zinc, iron and nickel leached from the Co-Cr-Mo alloy, whereas no traces of molybdenum, silicium, manganese or carbon were detected regardeless of how long the alloy was immersed in either of the three solutions (Table 1). The results of previous studies indicate that the ion release from an alloy doesn't necessarily correlate with the abundance of this element in the alloy. There is a selective dissolution so that the elements that are present in alloys only in traces can be released from them in larger amounts[8].

Zinc, iron and chromium leached the most when in phosphate buffer at pH 3.5 (reduced pH value under extreme conditions, Figures 2, 4, 5), whereas cobalt leached the most when in lactic acid at pH 3.5 (lowest end of pH under active plaque, Figure 1). During the initial period of exposure the nickel ions were released in all three solutions in very small amounts (10 μg/L) while increase in the ion release was observed on the sixth day in the phosphate buffer at pH 3.5. Significant nickel ions release also occurred on the 21st and 30th day in the phosphate buffer at pH 6.0 (lowest pH of freshly collected saliva) as well as in lactic acid at pH 3.5 (Figure 3).

TABLE 1
DECLARED COMPOSITION AND DETECTED METALS FROM THE Co-Cr-Mo DENTAL ALLOY LEACHED *IN VITRO*

Metal		Declared (%)	Detected
Cobalt	(Co)	64.0	Detected
Chromium	(Cr)	28.65	Detected
Molybdenum	(Mo)	5.0	Not detected
Silicium	(Si)	1.0	Not detected
Manganese	(Mn)	1.0	Not detected
Carbon	(C)	0.5	Not detected
Zinc	(Zn)	Undeclared	Detected
Iron	(Fe)	Undeclared	Detected
Nickel	(Ni)	Undeclared	Detected

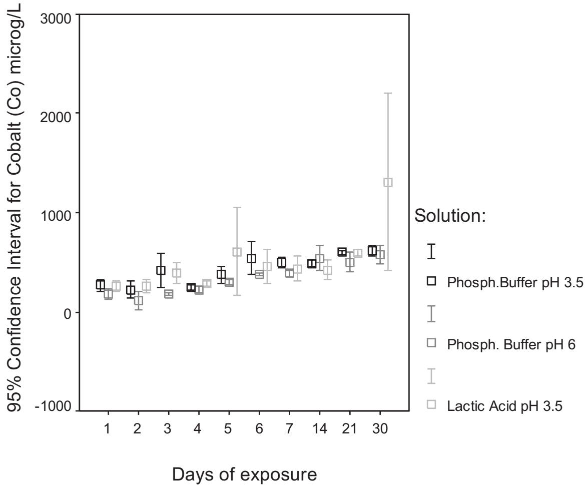

Fig. 1. Confidence interval (95%) for the release of cobalt (Co) ions into solutions of different composition and pH values over different time periods.

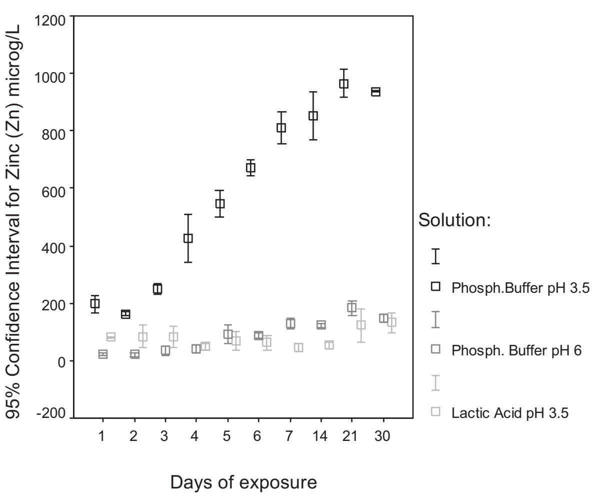

Fig. 2. Confidence interval (95%) for the release of zinc (Zn) ions into solutions of different composition and pH values over different time periods.

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 the favourable daily dietary intake[9,10]. The results of most recent epidemiological

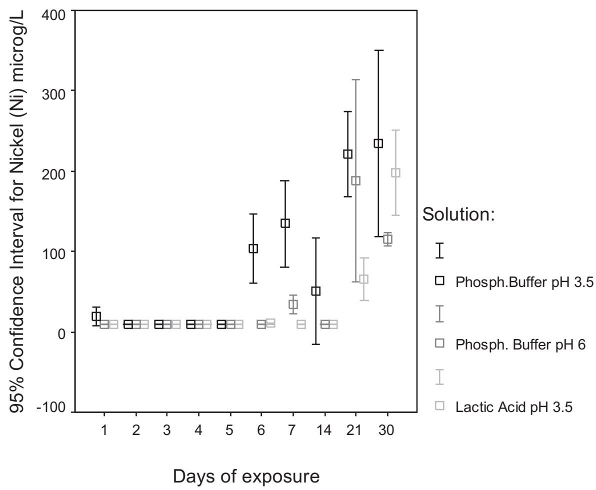

Fig. 3. Confidence interval (95%) for the release of nickel (Ni) ions into solutions of different composition and pH values over different time periods.

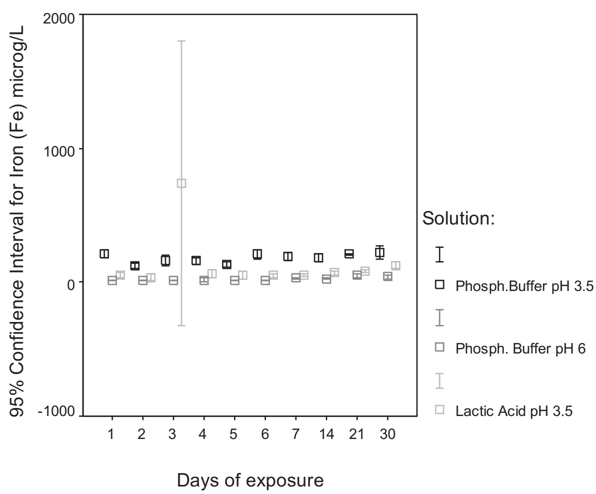

Fig. 4. Confidence interval (95%) for the release of iron (Fe) ions into solutions of different composition and pH values over different time periods.

studies indicate to the fact that cobalt, chromium and nickel, which are released from dental alloys, are metals which most often produce allergic responses[11]. Patch testing has been carried out on a large number of patients, subsequently resulting in positive reactions to some components of dental alloys, particularly to

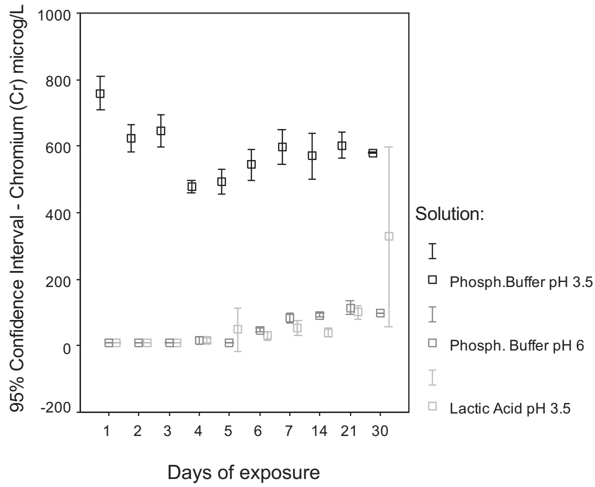

Fig. 5. Confidence interval (95%) for the release of chromium (Cr) ions into solutions of different composition and pH values over different time periods.

those containing nickel and chromium[12]. Allenby and Goodwin determined that the rate of 112 ppm of Ni (<0.05% nickal-sulfat) was needed to obtain a positive allergic reaction[13]. Peltonen noted that women were ten times more sensitive to Ni compared to men[14]. In 1984 the ADA workshop on the biocompatibility of metals in dentistry stated that sensitivity to chromium results from contact with chromate salts, which result from the corrosion of such alloys[15]. Experimental studies of chromium carcinogenesis in animals have been extensively investigated. As a trivalent ion, chromium appears to be of great biologic value and merit, forming part of the glucose tolerance factor. As a hexavalent ion, chromium can penetrate cells easily and is known to be a potent mutagenic and carcinogenic agent at low concentrations[16].

The leaching of metal ions from the tested Co-Cr-Mo alloy in the solution was dependent both upon the nature of the solution where the alloy was immersed and the duration of the immersion.

Multivariate analysis of variance revealed the time and solution (pH) related significant difference for each of the registered metal ions (Co, Cr, Zn, Fe, Ni) release ($p<0.001$). The concentrations of all recorded ions increased slowly during the time of exposure. Some studies which examined the ion release from different alloys over several months, showed that the amount of released ions was high at the beginning of the examination. After a proper time, a balance was established with linear ion release in relation to time[17].

New dental materials for clinical use are considered as medical devices and have to meet stringent safety and efficacy requirements. Dental alloys for cast restorations are of concern where materials remain in constant contact with living tissues. The American National Standard Institute (ANSI) / American Dental Association (ADA) provides guidelines to examine safety and biocompatibility of new dental alloys for cast restorations[18].

Ion release, as recorded in this study, showed that some metal ions could be detected from the examined alloy, although they are not declared by the manufacturer in all examined pH values (pH 3.5, as well a in pH 6)[19–21]. All detected elements are fortunatelly esential and are usually lacking in the dict of old people[9,10]. Concentration of Ni and Cr exceeded favourable daily intake, but were far bellow toxic limits. Their allergogenic potential must also be considered. Today, the knowledge of biocompatibility of different metal ions in dental alloys is fundamentally important to ensure the health od patients.

REFERENCES

1. CAREK, V., M. EGER, R. POŽGAJ, N. HORŠ, Acta Stom. Croat., 26 (1992) 239. — 2. WANG, R.R., Y. LI, J. Prosthet. Dent., 80 (1998) 495. — 3. PHILLIPS, R.W., E.W. SKINNER: Elements of dental materials (W.B. Saunders, Philadelphia, London, 1965). — 4. JOHANSSON, B.I., J.E. LEMONS, S.Q. HAO, Dent. Mater., 5 (1989) 324. — 5. MEZGER, P.R., A.L.H. STOLS, M.M.A. VRIJHOEF, E.H. GREENER, Dent. Mater., 5 (1989) 350. — 6. MORRIS, H.F., J. Prosthet. Dent., 58 (1987) 1. — 7. BERGMAN, M., B. BERGMAN, R. SÖREMARK, J. Oral. Rehabil., 7 (1980) 325. — 8. WATAHA, J. C., R.G. CRAIG, C.T. HANKS, J. Dent. Res., 70 (1991) 1014. — 9. SEIFERT, M., M. ANKE, Trace Elements and Electrolytes, 16 (1999) 17. — 10. ANKE, M., M. GLEI, R. MÜLLER, W. DORN, J. VORMANN, S. ANKE, J. Commodity Sci., 39 (2000) 119. — 11. FRANZ, G., The frequency of allergy against dental materials. Abstract 19, In: Procceedings. (International Congress on Biomaterials in Stomatology, Pretoria, South Africa, 1981). — 12. DOOMS-GOOSSENS, A., A. CEUTERICK, N. VANMAELE, H. DEGREEF, Dermatologica 160 (1980) 249. — 13. ALLENBY, C.F., B.F. GOODWIN, Cont. Derm., 9 (1983) 491. — 14. PELTONEN, L., Cont. Derm., 5 (1979) 27. — 15. National Institute of Dental Research, J. Am. Dent. Assoc., 109 (1985) 469. — 16. ROE, F.J.C., R.L. CARTER, Br. J. Cancer., 23 (1969) 172. — 17. WATAHA, J.C., P.E. LOCKWOOD, Dent. Mater., 14 (1998) 158. — 18. ANSI/ADA Specification No. 41 for recommended standard practices for biological evaluation of dental materials. (ANSI/ADA Specifications. Chicago, 1993) 401. — 19. RINČIĆ, N., A. ČELEBIĆ, I. BAUČIĆ, J. STIPETIĆ, E. PROHIĆ, S. MIKO. Acta Stom. Croat., 37 (2003) 5. — 20. MIKO, S., A. ČELEBIĆ, I. BAUČIĆ, Al. ĆATIĆ, N. RINČIĆ, M. BAUČIĆ, J. STIPETIĆ, Coll. Antropol., 26 Suppl. (2002) 136.- 21. STIPETIĆ, J., I. BAUČIĆ, M. BAUČIĆ, N. RINČIĆ, Al. ĆATIĆ, B. MOMČILOVIĆ, A. ČELEBIĆ. Coll. Antropol., 26 Suppl. (2002) 196.

Nives Rinčić

Nova cesta 134, 10000 Zagreb, Croatia

KOROZIJSKO PONAšANJE Co-Cr-Mo SLITINE U OTOPINAMA RAZLIčITOG SASTAVA I RAZLIčITIH PH VRIJEDNOSTI

SAŽETAK

Svrha ovog rada bila je ispitati ponašanje Co-Cr-Mo slitine u otopinama različite pH vrijednosti i različitog sastava kroz dulje vremensko razdoblje. Co-Cr-Mo slitina *in vitro* je bila izložena otopini koja je oponašala ljudsku slinu (fosfatni pufer pH 6.0), kiseloj otopini koja je oponašala ekstremne uvjete u usnoj šupljini (fosfatni pufer pH 3.5) i otopini mliječne kiseline čija pH vrijednosti odgovara uvjetima koji nastaju ispod dentobakterijskog plaka (mliječna kiselina pH 3.5). Uzorci ispitivane slitine uronjeni su u odgovarajuće otopine kroz 1, 2, 3, 4, 5, 6, 7, 14, 21 i 30 dana. Otopine su analizirane pomoću ICP-AES. Analiza je pokazala da su se tijekom mjesec dana iz ispitivanih uzoraka slitine otpustili ioni kobalta (Co), kroma (Cr), željeza (Fe), cinka (Zn) i nikla (Ni) i to u sve tri otopine. Rezultati ovog ispitivanja ukazuju na to da otpuštanje iona Co, Cr, Fe, Zn i Ni ovisi o sastavu otopine kojoj je slitina bila izložena, te o vremenu kroz koje je slitina bila izložena otopini ($p<0.001$).

Ključne riječi: pH vrijednost, korozija CoCrMo legure, vrijeme ekspozicije