

Karolina BEER-LECH
Barbara SUROWSKA

RESEARCH ON RESISTANCE TO CORROSIVE WEAR OF DENTAL CoCrMo ALLOY CONTAINING POST-PRODUCTION SCRAP

BADANIE ODPORNOŚCI NA ZUŻYCIE KOROZYJNE STOMATOLOGICZNEGO STOPU CoCrMo ZAWIERAJĄCEGO ZŁOM POPRODUKCYJNY*

Use of metal base dental prostheses is accompanied by not only wear due to biomechanical loads that occur during the process of chewing, but also by corrosive wear occurring in aggressive oral environment. Corrosive wear of metal elements of prosthesis may result in excluding it from further use by the occurrence of allergic or even carcinogenic reactions in patient, resulting from the release of toxic metal ions into the body. A common practice in prosthetic laboratories used in order to reduce production costs of dental prostheses is using so-called post-production scrap to subsequent castings. This scrap constitute the elements of casting channels, defectively made skeletons of prostheses or metal residues after prosthetic treatment. Use of post-production scrap to manufacture components to fulfill such high performance criteria (presence of complex biomechanical loads), and in particular taking into account the evaluation of biocompatibility, is the subject of discussion not only in the environment of scientists, but also the producers of dental alloys. The aim of the study was to investigate resistance to corrosive wear of dental cobalt alloy containing post-production scrap. The commercial dental alloy Wironit extra-hard with cobalt matrix has been used in this research. The study was based on a conducted polarity by means of potentiodynamic method in a solution of artificial saliva. Tested alloy samples, containing different percentage intake of post-production scrap, were cast by two casting methods - centrifugal and vacuum-pressure. Average values of parameters of Wironit extra - hard alloy resistance to corrosive wear: corrosion potential – E_{cor} , corrosion current I_{cor} , polarisation resistance R_{pol} and pitting potential – E_{pit} were determined. In order to assess alloy surface after corrosion microscopic observation was made. The results of research confirm high resistance of alloy to corrosive wear in environment of artificial saliva. Castings made using centrifugal methods provide lower current density in the passive state than those carried out by vacuum – pressure method, which suggests greater durability of passive layer confirmed by analysis of microstructure of samples after corrosion. Determination of correlation between content of post-production scrap and resistance to corrosion is ambiguous.

Keywords: corrosive wear, cobalt alloys, post-production scrap.

Eksploatacji stomatologicznych protez na podbudowie metalowej towarzyszy nie tylko zużycie wskutek obciążeń biomechanicznych, występujących podczas procesu żucia, ale również zużycie korozyjne mające miejsce w agresywnym środowisku jamy ustnej. Zużycie korozyjne metalowych elementów protezy skutkować może wyłączeniem jej z dalszego użytkowania wskutek wystąpienia u pacjenta reakcji alergicznych lub nawet nowotworowych, będących rezultatem uwalniania do organizmu toksycznych jonów metali. Częstą praktyką w laboratoriach protetycznych stosowaną w celu obniżania kosztów produkcji protez jest stosowanie tzw. złomu poprodukcyjnego do kolejnych odlewów. Złom ten stanowią elementy kanałów odlewniczych, wadliwie wykonane szkielety protez bądź metalowe pozostałości po obróbce protetycznej. Zastosowanie złomu poprodukcyjnego do wytwarzania elementów mających spełniać tak wysokie kryteria eksploatacyjne (występowanie złożonego stanu obciążeń biomechanicznych), a zwłaszcza biorąc pod uwagę ocenę biokompatybilności otrzymanych wyrobów, jest tematem dyskusyjnym nie tylko w środowisku naukowców, ale również i samych producentów stopów stomatologicznych. Celem pracy było zbadanie odporności na zużycie korozyjne stomatologicznego stopu kobaltu zawierającego złom poprodukcyjny. Do badań zastosowano komercyjny stop stomatologiczny Wironit extra – hard na osnowie kobaltu. Badanie polegało na przeprowadzeniu polaryzacji metodą potencjodynamiczną w środowisku roztworu sztucznej śliny. Próbkę stopu poddane badaniu, zawierające różny udział procentowy złomu poprodukcyjnego, odlane zostały dwiema metodami odlewniczymi - odśrodkową i próżniowo-ciśnieniową. Wyznaczono średnie parametrów określających odporność stopu Wironit extra – hard na zużycie korozyjne: potencjał korozji – E_{kor} , prąd korozji I_{kor} , opór polaryzacyjny R_{pol} i potencjał przebicia – E_{pit} . W celu oceny powierzchni stopu po korozji dokonano obserwacji mikroskopowych. Wyniki badań potwierdzają dużą odporność stopu na zużycie korozyjne w środowisku sztucznej śliny. Odlewy wykonane za pomocą metody odśrodkowej cechują się niższą gęstością prądu w stanie pasywnym niż te wykonane metodą próżniowo – ciśnieniową, co sugeruje większą trwałość warstwy pasywnej potwierdzoną analizą mikrostruktury próbek po korozji. Wyznaczenie zależności pomiędzy zawartością złomu poprodukcyjnego a odpornością na korozję jest niejednoznaczne.

Słowa kluczowe: zużycie korozyjne, stopy kobaltu, złom poprodukcyjny.

(*) Tekst artykułu w polskiej wersji językowej dostępny w elektronicznym wydaniu kwartalnika na stronie www.ein.org.pl

1. Introduction

CoCrMo alloys are some of the most popular alloys used in medical implants [8], and skeletal dentures but due to a combination of good mechanical properties, corrosion resistance and biocompatibility and favorable price and easy-to-treatment [3, 19].

Metal base skeletal dentures properties and their design would have a significant impact on their durability during their maintenance in the oral cavity [2]. Use of metal skeletons of dentures is accompanied not only by wear of fixing elements of prosthesis due to biomechanical loads that occur during the process of chewing, but also corrosive wear occurring in aggressive oral environment. Corrosive wear of prosthesis may result in excluding it from further use by the occurrence of allergic or even carcinogenic reactions in patient, resulting from the release of toxic metal ions into the body.

A common practice in prosthetic laboratories, allowing for a substantial reduction in the manufacturing cost of dentures, is the use of metals or their alloys, which has already been used in casting process [20, 21]. In the production process of metal skeletons of prostheses is produced a significant amount of post-production scrap constituting very often badly made castings, casting channels or which is residues after dental treatment. Use of post-production scrap to manufacture components to fulfill such high performance criteria of mechanical resistance (presence of state of complex biomechanical loads), and in particular taking into account the evaluation of biocompatibility, is the subject of discussion not only in the environment of scientists, but also the producers of dental alloys. Literature data indicate that performance characteristics of alloys containing post-production scrap may vary from factory alloys [1, 4, 6, 7, 11, 18]. Authors of research sometimes observe a change in chemical composition of alloy [4, 6] after use of secondary casting. These changes may affect connection strength of alloy with dental porcelain [11, 18], as well as affecting the growth of cytotoxicity of alloys [1] and affect the corrosion resistance [7].

Many manufacturers of dental alloys permit implementation of recasting, but with not less than 50% of intake of new material, provided that all the material must be from the same batch. Also, there is a manufacturer group, who does not allow recasting materials, or gives no information on the use of such dental alloys.

Corrosive wear of cobalt alloys as biomaterials was already the subject of many scientific studies, but mostly in the context of alloys intended for knee and hip joints implants, e.g. [5, 8, 17]. There is also a considerable group of research dealing with corrosive resistance of dental cobalt alloys, e.g. [12, 16].

Negligible number of research concerns the impact of addition of post-production scrap or secondary casting of metal on the resistance to corrosive wear [7, 9]. Furthermore, the views of authors of research on the prevalence of potential changes in resistance to corrosion, after applying in castings recasted materials, are contradictory.

The aim of the study was to investigate resistance to corrosive wear of dental cobalt alloy containing post-production scrap and identifying the impact of casting method on this type of wear.

2. Materials and methods

For research was applied commercial dental alloy – Wironit extra – hard from Bego Co. with the following chemical composition (by mass) – specified by the manufacturer: Co – 63 %, Cr – 30,01 %, Mo – 5.0 %, Si – 1.1 %, Mn, C<1.

From the alloy were cast samples in form of cylinders with a diameter of 5 mm. Precision casting technique by method of melt models was implemented. The silicone wax model primed with acrylic resin was placed in metal ring and

primed with refractory ceramic material (the so-called covering) with trade name Wirovest by Bego. After drying wax was melt in an oven at temperature of 523 K, then a form was heated to a temperature of 1223 K to sinter the form, to burn rests of wax and remove gases. The inductively melt inserts were cast by two methods: vacuum - pressure in Nautilus Bego device (samples marked with PC) and centrifugal in Rotocast casting machine by Roco Dental Equipment (samples marked with W). Ceramic crucibles were used. The casting temperature was in line with the alloy manufacturer's recommendations. For both methods it was 1693 K. Made casts contained respectively 0, 50 and 100% of factory alloy, supplemented with a sufficient amount of post-production scrap. The marking of samples is given in Table 1.

Table 1. The marking of samples for testing

No.	Casting method - vacuum - pressure	Casting method - centrifugal	Sample determination / the content of factory alloy
1.	0_PC	0_W	A sample containing 100% of post-production scrap
2.	50_PC	50_W	A sample containing 50% of factory alloy and 50% of post-production scrap
3.	100_PC	100_W	A sample containing 100% of factory alloy

The surface of the samples before the test has been subjected to a treatment consisting of grinding with abrasive papers of gradation equal to 220–1200 on rotary grinders and then mechanical polishing on diamond discs by Buehler with use of dedicated diamond suspensions MetaDi one by one (9 μm and 3 μm) and colloidal silica ~ 0.05-mm MasterMet), cleaning in ultrasonic washer in ethanol and dried with compressed air.

An assessment of resistance to corrosive wear was conducted by electrochemical method supported with quality observations of surface. For corrosive measurements was used electrochemical test-kit ATLAS 0531, consisted of potentiostat – galvanostat controlled by a computer and trielectrode electrochemical vessel placed in a Faraday cage. Trielectrode electrochemical vessel consisted of the tested electrode, which was consecutive samples of Wironit extra – hard alloy, a platinum auxiliary electrode and saturated calomel reference electrode with electrolytic bridged finished with a Luggin's capillary. In addition, this kit was equipped with a heater with thermostat and electromagnetic stirrer allowing to maintain temperature of measuring environment at a constant level of 310K (37°C) with a measuring accuracy of $\pm 0,5^\circ\text{C}$.

Measurement was taken in a solution environment of artificial saliva [14], the composition of which is given in Table 2.

During the tests current-voltage characteristics were recorded. Polarization was carried out with a speed change of potential equal to 1 mV/s in respect of the value of potential from -1000 to +1200mV. To determine characteristic values of E_{cor} , I_{cor} , R_{pol} and E_{pit} was used Atlas Lab software. It can be used to calculate the polarisation resistance from a sector of a curve along with corrosion potential, Tafel constants b_a and b_c , corrosion potential E_{cor} and corrosion current I_{cor}

Table 2. The composition of artificial saliva solution per 1 dm³ of solution

The composition of artificial saliva solution:	The amount in the solution [g]:
NaCl	0,4
KCl	0,4
NaH ₂ PO ₄ × H ₂ O	1,35
NaH ₂ P	0,78
Na ₂ S × 9 H ₂ O	0,005

and plotting Tafel curves. In addition, from polarisation curves, using „extrapolation” option was determined pitting potential E_{pit} . The average values for series of measurements were calculated using a modulus for mathematical analysis.

In addition, in order to compare the state of surface of the samples before and after corrosive was conducted microscopic observation using metallographic optical microscope Nikon MA100.

3. The results of research and discussion

The results of research (Figure 1 and 2, Table 3) show that Wironit extra-hard alloy has a very good ability to passivation expressed by broad passive area and low density of passivation current. In Figures 1 and 2 are presented the representative polarisation curves of Wironit extra – hard alloy samples carried out without the addition of post-production scrap. A similar shape of curves was also registered for samples containing post-production scrap.

Table 3 shows the results of the tests containing average values of the corrosion potential E_{cor} , corrosion current I_{cor} , polarisation resistance R_{pol} and potential, above which were formed corrosion pits (of pitting potential) E_{pit} .

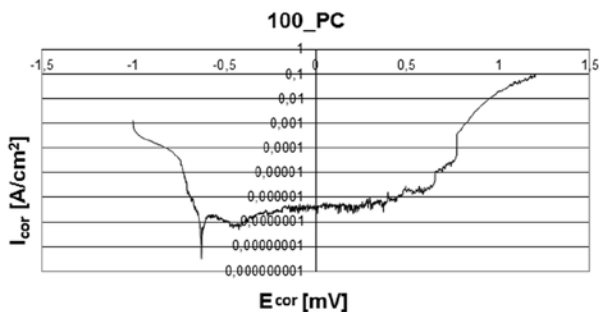


Fig. 1. The example of polarisation curve for sample 100_PC

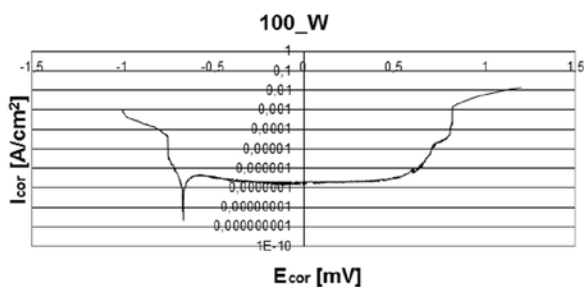


Fig. 2. The example of polarisation curve for sample 100_W

Table 3. The results of the tests of electrochemical corrosion of Wironit extra - hard alloy

The content of manufacturing alloy [%]	\bar{E}_{cor} [mV]	\bar{I}_{cor} [A/cm ²]	\bar{R}_{pol} [Ω*cm ²]	\bar{E}_{pit} [mV]
0_PC	-673	$6,29 \cdot 10^{-7}$	57 667	442
50_PC	-486	$13,8 \cdot 10^{-7}$	152 850	593
100_PC	-561	$8,38 \cdot 10^{-7}$	90 125	603
0_W	-674	$14,4 \cdot 10^{-7}$	56 000	623
50_W	-406	$6,19 \cdot 10^{-7}$	196 000	620
100_W	-583	$5,92 \cdot 10^{-7}$	141 000	600

Data in Table 3 and in Figures 3 and 4 indicate the existence of differences in corrosive resistant of Wironit extra – hard alloy samples cast using two methods: vacuum-pressure and centrifugal, containing varying amounts of post-production scrap. Castings made by centrifugal method are characterized with greater durability of passive layer expressed by the lower current density in the passive state. These results do not confirm observation [13, 15], that the marginal impact on dental alloys corrosion resistance has the casting method used, and only chemical composition of these alloys decide on their resistance to corrosive wear. Comprehensive research of macro- and microstructure of castings described by the author in earlier publications [3, 20] indicate, however, the observed dependence of corrosion liability from a macro- and microstructure of alloys.

However, determining the best resistance of Wironit extra - hard alloy to corrosive wear due to the content of manufacturing alloy and post-production alloy is not clear.

Due to the corrosion potential the best parameters (the highest value of E_{cor}) show castings containing 50% of factory alloy with corrosion potential E_{cor} equal to -486 mV for 50_PC and -406 mV for 50_W. The next in order are castings made of factory alloys, the smallest values of the corrosion potential has been reported for samples from both methods performed fully from post-production scrap. However, taking into account the value of the corrosion current I_{cor} most favourable properties indicate successively castings 100_W, where I_{cor} is $5,92 \cdot 10^{-7}$ A/cm², 50_W ($I_{cor} = 6,19 \cdot 10^{-7}$ A/cm²) and 0_PC ($6,29 \cdot 10^{-7}$ A/cm²). Polarization resistance of vacuum-pressure and centrifugal method showed the highest value for samples containing 50% of factory alloy, while average the greatest pitting potential E_{pit} for vacuum-pressure method for samples 100_PC – 603 mV, and for centrifugal method for samples 0_W – 623mV.

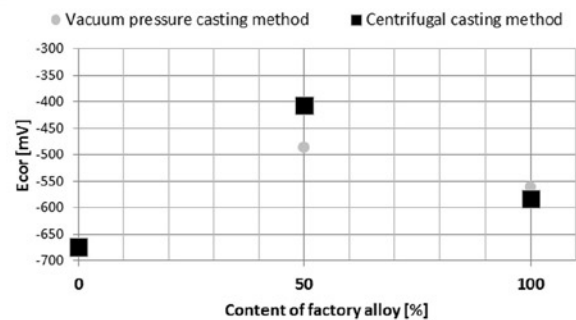


Fig. 3. The value of mean corrosion potential for samples with different content of factory alloy made by vacuum – pressure and centrifugal method

Figure 5 shows dendritic microstructure of samples without addition of post-production scrap cast by vacuum – pressure and centrifugal method. In the structure have been found casting defects (5a and b) in form of porosity. Microstructures of the same casts after corrosive research are shown in Figure 6. The dendritic structure of samples after the test has been more highlighted. Present passive layer, particularly clearly visible in Figure 6a, is not continuous.

The casting defects occurring in the structure contribute to the development of surface, ingress of aggressive environment and make difficult uniform deposition of passive layer being a cause of increased corrosion, what is known from the literature [10]. Also interdendritic segregations in block form are described in greater detail in [20], not covered with oxide layer due to difference of potentials, may initiate the occurrence of corrosion pits.

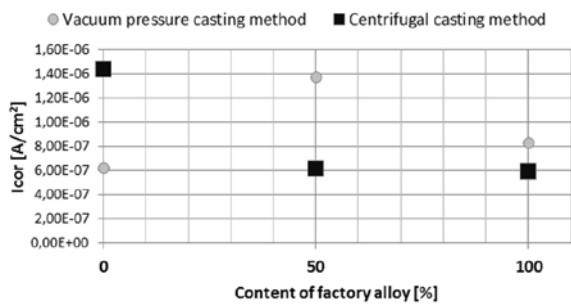


Fig. 4. The value of mean corrosion current for samples with different content of factory alloy made by vacuum – pressure and centrifugal method

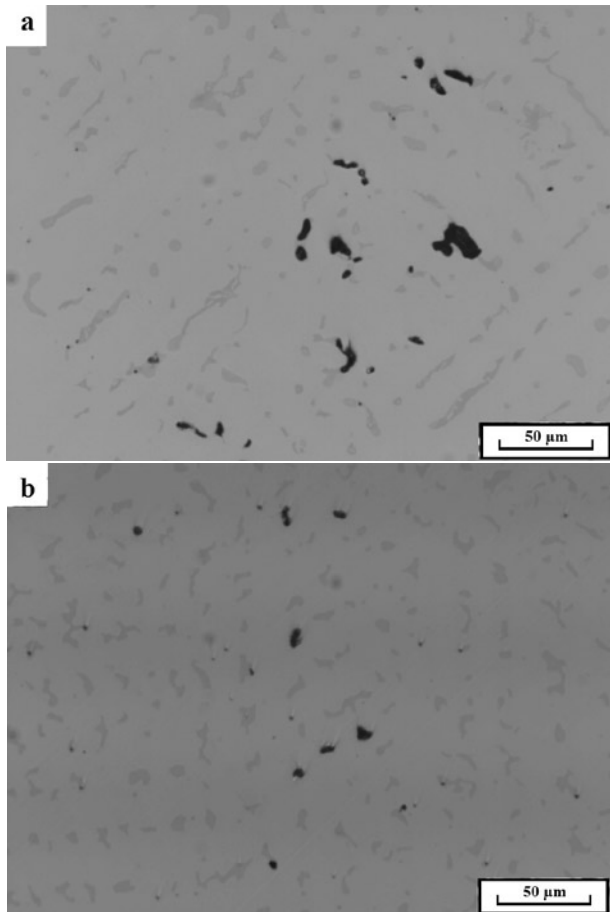


Fig. 5. The microstructure of Wironit extra – hard alloy before the test: a) the sample 100_PC; b) the sample 100_W

Observations of samples indicate the occurrence of corrosion pits and damage to the surface in form of intergranular corrosion (the darkest areas in the figures). These pits, created after a pitting of passive layer, occur on the borders of block precipitates (Figure 6a and b), in these precipitates (6b) and in the interdendritic areas along continuous precipitates (Figure 6b). This is most likely related to chromium zone segregation in the samples. This element, responsible for corrosion resistance in Co-Cr -Mo alloys, in accordance with the results [12], dominates in the block precipitates, as shown by previous research of the authors [20], while the boundaries between precipitates and matrix are depleted in this element. Greater number of pits was observed for vacuum-pressure method, which is consistent with the results of electrochemical measurements.

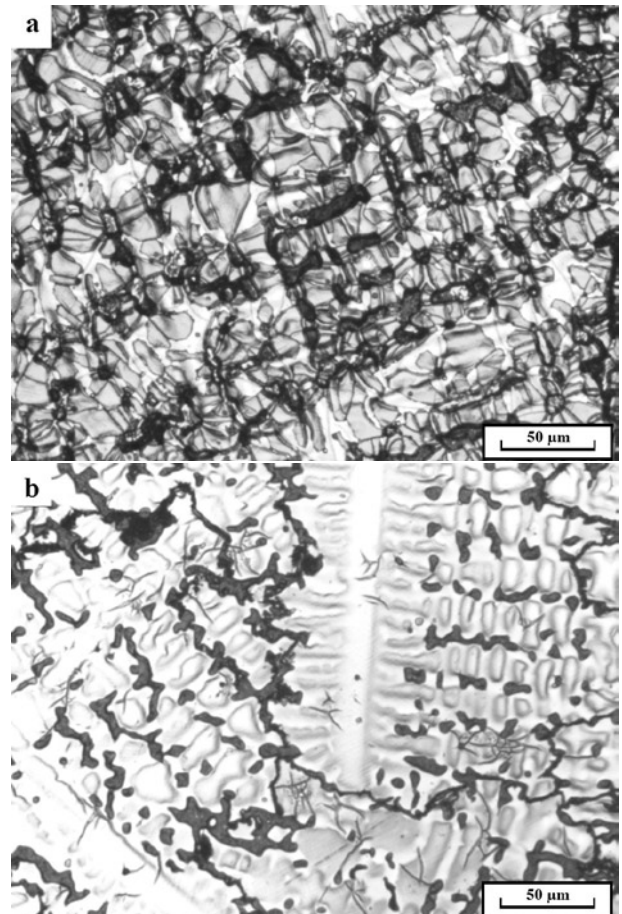


Fig. 6. The microstructure of Wironit extra-hard alloy after the test on electrochemical corrosion: a) the sample 100_PC; b) the sample 100_W

The presented results confirm that problem of resistance changes to corrosive wear of dental CoCrMo alloys after applying of post-production scrap is a complex issue and worth further research in order to obtain convincing proof whether implementation of recastings has actually a significant effect on dental alloys corrosion resistance, as pointed out [7] or rather marginal [9].

4. Conclusions:

Research on resistance to corrosive wear of Wironit extra - hard alloy showed high resistance of alloy to electrochemical corrosion in artificial saliva solution. This alloy has a very good passivation ability, and broad passive area, and low current density in the passive state. Castings made using the centrifugal method demonstrate higher durability of passive layer expressed by lower passivation current than castings made by vacuum pressure method. However, determination of dependence of resistance of Wironit extra - hard alloy to corrosive wear from manufacturing alloy content and post-production scrap is not possible without taking into account other factors (changes of chemical composition, microstructure, macrostructure).

Acknowledgements:

The paper was created in the course of the project of National Science Center „Preludium” No. 2011/01/N/ST8/07774. Authors are grateful for Professor Janusz Borowicz, MD, Ph.D. for assistance in preparation of samples for testing.

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Karolina BEER-LECH**Barbara SUROWSKA**

Department of Materials Engineering

Faculty of Mechanical Engineering

Lublin University of Technology

ul. Nadbystrzycka 36, 20-618 Lublin, Poland

E-mails: k.beer@pollub.pl, b.surowska@pollub.pl
