

The Influence of Remelting on the Quality of Prosthetic Cobalt Alloys

M. Nadolski^a*, M. Łągiewka^a, Z. Konopka^a, A. Zyska^a, G. Golański^b

 ^a Foundry Department, Czestochowa University of Technology,
^b Institute of Materials Engineering, Czestochowa University of Technology, Al. Armii Krajowej 19, 42-200 Częstochowa, Poland
* Corresponding author. E-mail address: nadolski@wip.pcz.pl

Received 26.06.2015; accepted in revised form 20.07.2015

Abstract

A commercial cobalt alloy applied in dental prosthetics was investigated. The scope of the work included the microstructure analysis, performance examination (tensile strength, microhardness, corrosion resistance), and dilatometric examination. The investigated alloy after a single remelting was characterised by higher tensile strength and hardness. There were not found the definite results with regard to the corrosion resistance of the examined materials. No significant change occurred in the coefficient of thermal expansion.

Keywords: Cobalt, Centrifugal casting, Lost wax technology

1. Introduction

A significant amount of metal scrap, consisting mainly of the gating system, arises during the manufacturing of prosthetic castings. The scrap includes also the defected, incorrect castings. It should be noticed that some melting techniques used in prosthetic workshops promote the occurrence of casting defects. The melting process carried out by heating the alloy with gas burner or by induction heating of the charge of mass not exceeding 100 g proceeds relatively quickly, but makes impossible the reliable temperature measurement and control [1, 2]. After melting, the alloy is cast in moulds made according to the investment casting technology, either by centrifugal casting or by the vacuum-pressure casting.

The very probable danger of casting defect occurrence [3-9] fostered the development of alternative methods, using the Computer Aided Design / Compute Aided Manufacturing (CAD/CAM) approach. The method meets the demand for the thin-walled elements reproducing the human mouth anatomy which can be easily reproduced during prosthetic works [10, 11].

The change in production method concerning the metal part of the denture yielded the change in many elements of the process, which now consist in taking the impression of a dental arch, 3D scanning of the achieved study model, processing of the results with application of graphic programs, milling of metal, repeated applying and sintering of ceramic layers which imitate teeth material and colour. The technological problems resulting both from the requirements imposed on biomaterials and from the necessity of providing adequate mechanical integrity of the meta/ceramic bond are still the same, but another problem arises with regard to the massive metal waste, which cannot be further processed by milling, though the amount of the remaining material can reach up to 60% of the expensive initial plate.

Therefore it is interesting to consider if such a waste can be reused as a charge material for producing prosthetic casting.

According to the information given/supplied by the producers of the prosthetic casting alloys, it is allowable to use the charge containing up to 50% of home scrap. Such a fraction, according to the information, does not result in the lowered quality of products [12]. This information concerns mainly the cobalt casting alloys and the noble metal alloys [13]. However, the laboratory search concerning the influence of the conditions and the number of repetitions of the re-melting process on the quality of the prosthetic casting alloys, lead to different, sometimes even contrary conclusions. Some of the reports indicate the change in chemical composition of the examined alloys [14, 15], others point to the accelerated corrosion process [16, 17], as well as to the reduced [17, 18] or increased [15, 19] mechanical properties. Some authors state no significant influence of the factors under consideration on mechanical properties of the produced castings [20].

Moreover, there are many other demands, which prosthetic alloys - also the remelted ones - should meet. They should be biocompatible, i.e. should not have toxic or allergic effects on a human body. They should be also corrosion-resistant and should not get tarnished in the mouth environment [21, 22]. They should be relatively cheap and easily workable. Therefore the nickel-free cobalt alloys found many practical applications in the production of metal skeletons of the removable partial dentures and fixed metal/ceramic prostheses (bridges) [23]. The applied alloys should exhibit the coefficient of thermal expansion (α) as close as possible to the coefficient of the ceramic material, because they are subjected to multiple heating and cooling cycles during the application of the ceramic layers. Their hardness on the one hand determines the easiness of the final machining, on the other hand it controls their resistance to scratching [23].

The paper presents the results of the initial research work with respect to the possibility of applying the waste of the material originally intended for CAD/CAM milling in prosthetic casting methods.

2. The material and the methods of examination

The investigated material was a prosthetic cobalt alloy of chemical composition presented in Table 1.

Table 1.

|--|

| Со | Cr | Si | W | Others | |
|-------|-------|------|------|-----------|--|
| 63.00 | 24.00 | 1.33 | 8.00 | Mo, Nb, C | |

The alloy is intended for dental prostheses made by CAD/CAM methods. The material was first examined in the 'as bought' conditions (material No. 1), in order to compare the results with the results achieved for the remelted material (material No. 2). The remelting was carried out by induction heating. After achieving the liquid state the specimens were cast under the centrifugal pressure by means of a centrifugal casting machine. The mould was prepared using wax patterns (Fig.1) according to the investment casting technology as the block mould made of the phosphate bonded sand. The mould temperature at the moment of pouring was equal to about 950°C. Castings were left in the mould until they cooled down to the room temperature.

The performed examinations of mechanical properties consisted in the tensile strength R_m measurement, completed



Fig. 1. Wax patterns of the tensile specimens

during the tensile test carried out in accordance with PN-01/H-04310 Standard. The test was performed by means of the computer-controlled Zwick 1488 universal tester at the following set of parameters: the initial stress -1 MPa, strain rate -7 mm/min, maximum breaking force -10 kN. The value of the breaking force P was recorded during the tensile test, as well as the elongation Δl .

The observation and the recording of microstructure images were performed by means of the optical microscope Axiovert 25 (OM) on the prepared microsections. Microhardness was measured according to Vickers method by means of Future-Tech FV-700 microhardness tester under the indenter load of 0.5 kG (4.903 N).

Dilatometric measurements were taken within the temperature range from 30°C to 1000°C for the specimens of 4 mm diameter and about 32 mm length. The heating and cooling rate was equal to about 0.26 K/s. The assumed heating and cooling cycle corresponds to the sintering process of the applied prosthetic porcelain. The measurements were taken by means of the DA-3 automatic dilatometer, and the purpose of the examination was to compare the dimensional changes occurring in the investigated CoCr alloys.

The examination of the corrosion resistance of the materials intended for implants was carried out in Ringer's solution at the temperature of 37° C. The chemical composition of the solution was as follows: 0.39 g of potassium chloride, 8.6 g of sodium chloride, and 0.48 g of calcium chloride per 1 dm³ of the solution. The electrochemical measurements were performed by means of digitally controlled model 7050 potentiostat made by AMEL, co-operating with the computer unit using Juniorassist program in the three electrode system. The reference electrode was the saturated calomel electrode (SCE), while the auxiliary electrode was a platinum wire; the examined specimens were used as working electrodes. The applied potential was changed during the experiment from cathode values towards the anode values, within the range from -2.0 V to 5.0 V with respect to SCE. The most representative polarization curves were selected

for the analysis of corrosion resistance of the examined materials.

The polarization curves served as a basis for the determination of parameters characterizing the material susceptibility to corrosion: the corrosion potential E_{kor} , and the corrosion current density I_{kor} .

The X-ray structural examination were carried out by means of SEIFFERT XRD 3003 T-T diffractometer using cobalt lamp emitting radiation of wavelength $\lambda = 0.17902$ nm.

3. Results of examinations

The result of tensile strength measurement obtained for the specimens cast in the phosphate bonded sand moulds reached about 860 MPa, what gives the increase by about 15% in comparison with the tensile strength of the initial material.

The microhardness measurement taken at the cross-sectional microsection of Co-Cr showed that the material microhardness prior to its remelting fell within the range $290\div323$ HV 0.5, while the remelted and cast material exhibited the value of $338\div361$ HV 0.5.

The increase in the R_m value could be caused by the way in which the melting process was carried out and/or by the solidification conditions which could change the structure of the alloy.

The performed X-ray quantitative structural phase analysis (Figures 2 and 3) revealed the occurrence of two main phases: the cobalt matrix (Co) and chromium carbides $Cr_{23}C_{6}$.





Observation of the microstructures of both of the investigated alloys revealed the characteristic dendritic structure. The material No. 1 contained multiple precipitates arranged either along the grain boundaries or within the interdendritic spaces (Fig. 4). An example of the morphology of precipitates is presented in Fig. 5. Sparsely distributed carbide precipitates observed in the cast material are arranged within the interdendritic spaces (Fig. 6) An example of the morphology of precipitates is presented in Fig. 7. It can be supposed that the low cooling rate fostered the solution of carbides in austenite grains, thus being responsible for the increase in mechanical properties of the material No. 2.



Fig. 4. Microstructure of the alloy No. 1



Fig. 5. Morphology of precipitates in the alloy No. 1





Fig. 7. Morphology of precipitates in the alloy No. 2

The polarization curves recorded for both materials are shown in (Fig. 8). Their analysis reveal that in the case of the remelted material (material No. 2) the value of corrosion current, which is a measure of corrosion rate in the applied enironment, is increased by almost one order in comparison with the value determined for the material No. 1 (Table 2). The course of the potentiokinetic polarization curves indicate that the material No. 1 undergoes passivation over a certain potential range. It is related to the arising of a protective layer, which produces the effect of reduced current values in the active region. Then, at the potential value of about 1.2 V versus SCE, a rapid increase in current value is observed, characteristic for the break-down of the passive layer and the loss of its protective properties (pitting corrosion).

The potentiometric curve recorded for the material No. 2 exhibits no rapid changes in current values and no loss of protective properties.

The recorded value of the corrosion potential of the material No. 1 takes a higher value than the one of the material No. 2, what suggests that its corrosion resistance is better than that of material No. 2. However, the characteristic values for the

material No. 2 were found from the cathodic curve only. Since the anodic curve is not possible to determine for the material No. 2, the corrosion rate could not be exactly found.



Fig. 8. Polarization curves registered for investigated materials

Table 2.

The results of electrochemical measurements carried out for Co alloys obtained from the recorded potentiokinetic polarization curves

| Alloy | E_{kor} versus SCE V | I_{kor} mA*mm ⁻² |
|-------|------------------------|-------------------------------|
| No. 1 | -0.198 | 0.0397 |
| No. 2 | -0.892 | 0.0089 |

The course of the expansion of the materials No. 1 and No. 2 is of a linear character (Fig. 9.), not indicating any polymorphic transformation for either of the alloys within the examined temperature range. However, it differs slightly due to a difference in the value of the coefficient of thermal expansion (α), as shown in Table 3.



Fig. 9. Dilatometric curves of materials No. 1 and 2

Table 3. Coefficient of thermal expansion α

| Temperature range | $\alpha \times 10^{-6} \text{ K}^{-1}$ | | |
|-------------------|--|-------|--|
| °C | 1 | 2 | |
| 30-600 | 13.71 | 14.27 | |
| 600-1000 | 13.17 | 13.89 | |

It was recognized that these values fall within the limits assumed for materials intended for ceramic coating in prosthetic works.

4. Conclusion

The examined alloy after single remelting was characterised by higher tensile strength and microhardness than the initial material. It results from the partial dissolving and refining of the $Cr_{23}C_6$ carbide precipitates, which is mirrored by their changed arrangement.

Since the data are insufficient to determine the exact corrosion rate, the further study of this problem seems to be reasonable.

The coefficients of thermal expansion determined for the commercial alloy and for the alloy after a single remelting operation do not exhibit significant differences.

References

- Hajduga, M. & Jasiński, M. (2008). The influence of melting technology on the structure of metallic materials. *Modern Dental Technician (Nowoczesny Technik Dentystyczny)*, 1, 53-57. (in Polish).
- [2] Marciniak, S., Połomski, J., Pierzynka, R., Marciniak-Kraul, K. & Fabjański, P. (2009). The assessment of casting systems. *Modern Dental Technician (Nowoczesny Technik Dentystyczny)*, 1, 44-49. (in Polish).
- [3] Peter, I., Rosso, M., Toppi, A., Dan, I. & Ghiban, B. (2013). Investigation on Cobalt based alloy modified by Titanium for dental applications, *Archives of Materials Science and Engineering, Volume 61, Issue 2, June*, 62-68.
- [4] Reclaru, L., Lüthy, H., Eschler, P.Y., Blatter, A., Loeffel, O., Zurcher, M.H. (2004). Cobalt-Chromium Dental Alloys Enriched with Precious Metals, *European Cells and Materials Vol. 7. Suppl.* 2, 51-52;
- [5] Prabhu, R., Geetha Prabhu, K.R., & Ilango, T. (2011). Dental Prosthesis: An Evaluation on Mechanical Properties of Recast Base Metal Alloys, *Journal of Clinical and Diagnostic Research. Vol-5(8), December*, 1682-1685;
- [6] Reinmann, L. & Dobrzański, L.A. (2013). Influence of the casting temperature on dental Co-base alloys properties, *Archives of Materials Science and Engineering, Vol. 60, Issue 1, March*, 5-12.
- [7] Dobrzański, L.A. & Reinmann, L. (2011). Influence of Cr and Co on hardness and corrosion resistance CoCrMo alloys used on dentures, *Journal of Achievements in*

Materials and Manufacturing Engineering, Vol. 49, Issue 2, Dec.

- [8] Komorek, Z., Jóźwiak, S. & Kuchta, M. (2006). The influence of the production conditions on the mechanical properties of Co-Cr-Mo-C dental alloy, *Archives of Foundry, Vol. 6, No 18(2/2)*, 279-282.
- [9] Majewski, S.W. (2007). New technologies of manufacturing the fixed dental prostheses: galvanoforming, CAD/CAM technology, titanium processing and modern ceramic systems. Nowe technologie wytwarzania stałych uzupełnień zębowych. *Dental Prosthetics (Protetyka Stomatologiczna), t. LVII, nr 2,* 124-131; (in Polish).
- [10] Gładkowska, M., Montefka, P. & Okoński. P. (2008). Comparison of CAD/CAM systems used in modern prosthodontics. *Dental Prosthetics (Protetyka Stomatologiczna), t. LVIII, nr 2,* 105-113.
- [11] Noack, F. (2012). CoCr-Revolution, Dental dialog. The International Journal of Dental Technology. Vol. 13 08, 2-6.
- [12] Strietzel, R. (2000). Recasting of dental alloys, *Dental-labor*, 4, 3-6. (in Polish).
- [13] Surowska, B., Beer, K., Veremchuk, I. (2011). Technological problems with production of metal skeleton elements of dental prostheses, *Advances in Science and Technology (Postępy Nauki i Techniki), 11*, 81-88, (in Polish).
- [14] Hajduga, M. & Puchalik, A. (2009). The serviceability assessment of Heraenium NA alloy after remelting in the light of structural examinations. *Modern Dental Technician. (Nowoczesny Technik Dentystyczny), 3*, 56-60. (in Polish)
- [15] Ameer, M.A., Khamis, E. & Al-Motlaq, M. (2004). Electrochemical behaviour of recasting Ni-Cr and Co-Cr nonprecious dental alloys, *Corrosion Science*, 46, 2825-2836.
- [16] Klimek, L., Pierzynka, R., Błaszczyk, T., Burnat, B., Scholl, H. & Marciniak, S. (2009). The effect of recasting on corrosion of DUCINOX prosthetic alloy, *Archives of Foundry Engineering*, 9, iss. 3, 67-70.
- [17] Peraire, M., Martinez-Gomis, J., Anglada, J.M., Bizar, J., Salsench, J. & Gil, F.J. (2007). Effects of Recasting on the Chemical Composition, Microstructure, Microhardness, and Ion Release of 3 Dental Casting Alloys and Titanium, *The International Journal of Prosthodontics*, 20, 286-288.
- [18] Henriques Guilherme, E.P., Consani, S., de Almeida Rollo João, M.D. & Andrade e Silva, F. (1997). Soldering and remelting influence on fatigue strength of cobalt-chromium alloys, *The Journal of Prosthetic Dentistry*, 78, 146-152.
- [19] Bauer, J., Cella, S., Pinto, M.M., Costa, J.F., Reis, A. & Loguercio, A.D. (2010). The use of recycled metal in dentistry: Evaluation of mechanical properties of titanium waste recasting, Resources, *Conservation and Recycling*, 54, 1312-1316.
- [20] Pierzynka, R., Marciniak, S. & Klimek, L. (2010). The influence of the number of remeltings on mechanical properties of DUCINOX alloy, *Modern Dental Technician* (*Nowoczesny Technik Dentystyczny*), 2, 22-24. (in Polish).
- [21] Łukaszczyk, A. & Augustyn-Pieniążek, J. (2015). Corrosion Resistance of Co-Cr-Mo Alloy Used in

Dentistry, Archives of Metallurgy and Materials, Vol. 60, Issue 1, 523-528.

- [22] Klimecka-Tatar, D., Radomska, K. & Pawlowska, G. (2015). Corrosion Resistance, Roughness and Structure of Co64Cr28Mo5(Fe, Si, Al, Be)3 and Co63Cr29Mo6.5(C, Si, Fe, Mn)1.5 Biomedical Alloys, *Journal of the Balkan Tribological Association Vol. 21, No 1*, 204–210.
- [23] Beer-Lech, K., Szala, M., Piskorska, P., Majewski, Ł. (2013). Examination of castability and hardness of the cobalt-based dental casting alloy. Materials Engineering, Selected problems of materials engineering, Lublin: Lublin University of Technology, 105-122; (in Polish).