Cobalt-Chromium Dental Alloys

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Contributor: Willi Andrei Uriciuc , Adina Bianca Boșca , Anida-Maria Băbțan , Horațiu Vermeșan , Cecilia Cristea , Mihaela Tertiș , Petru Pășcuță , Gheorghe Borodi , Maria Suciu , Lucian Barbu-Tudoran , Cătălin Ovidiu Popa , Aranka Ilea

The processing of Co–Cr alloys by melting and casting in refractory molds remains a viable method that can support innovation, in the context of technology advance in recent years towards digitalization of the manufacturing process, i.e., the construction of prosthetic frameworks conducted by additive methods using Co–Cr powder alloy.

cobalt–chromium dental alloys casting corrosion biomaterials oxide layers

1. Introduction

In dentistry, oral rehabilitation treatments are performed using prosthetic works that restore the masticatory function, and, from a constructive point of view, their stability must be ensured by resistance frameworks, which are currently made of metallic materials, such as Cobalt–Chromium (Co–Cr) alloys [1]. Dental restorations represent just a part of biomaterial applications in dentistry when adhesion aspects and surface modifications strongly influence the functionality of medical devices [2].

Metallic materials are considered materials of choice in the manufacture of prosthetic frameworks. Co–Cr alloys, or stellites, are commonly used in dental prosthetics [3]. There are different types of metal corrosion: inter-granular, pitting, crevice, fatigue, stress, fretting, and galvanic. On the other hand, in many cases (such as metal-on-metal prosthesis) corrosion and wear appears between two metallic components [4]. The accessibility of the classical method of processing Co–Cr alloys by melting and casting gives these alloys a wide range of uses [5].

The method of manufacturing prosthetic frameworks by melting and casting Co–Cr alloys depends on the refractory shape and its deformation after heat treatment. Regardless of whether the model of the complementary structure was made on a duplicate refractory model or directly on the assembly surface, the method is influenced by the refractory material [6]. Although the refractory packing mass is specific to the molded alloy, in terms of the expansion on heating and the shrinkage on cooling of the materials, the complementary frameworks made by this method require adaptation by mechanical processes at the surfaces [7].

In order to perform a better dental application by casting, the cobalt–chromium alloy must have a homogenous and dendritic structure, without inclusions, which is possible when is used casting technology in protective controlled environment [8].

2. Corrosion at the Surface of Co–Cr Alloys

The biocompatibility of dental alloys is a critical issue, because the alloys remain in long-term intimate contact with tissues and saliva [9] on the oral cavity that represents the prosthetic field [10][11]. To ensure biological safety [12], the most important property of alloys is resistance to corrosion in the oral cavity [13], where the alloys are exposed to a variation of pH, influenced by the nature of food and dental plaque. A low pH increases the release of metallic elements, acting as a corrosive medium [14].

The corrosion resistance of the surface of a metal prosthetic structure is the most important feature in the evaluation of the biocompatibility of the alloy [15]. The majority of stellites used in dentistry contain about 60% Co and 25% Cr, which ensure the biocompatibility of the alloy. Alloys may also contain small amounts of molybdenum (Mo), tungsten (W), and other metals [10][16].

Cobalt and chromium form a solid solution if the latter is found up to about 30%, according to the Co–Cr diagram. A value of 30% represents the solubility limit of Cr in Co. Exceeding this value makes the additional percentage of Cr to be found in the σ phase, in which it is extremely fragile, imprinting this feature on the entire alloy. For higher percentages of Cr, higher corrosion resistance is reached by these alloys [14][15][16].

Cr is the main alloying element, responsible for imprinting the passive character of the alloy. Added in a proportion of 11–33%, Cr increases the chemical stability of the alloy by forming a protective surface of oxide films. Cr improves resistance to oxidation at high temperatures, thus protecting the alloy against corrosion [15].

Cr forms oxide (Cr_2O_3) films, which are stable and adherent with a protective property, ensuring the minimization of the diffusion speed of metal ions at the surface. The resistance of alloys to chemical agents that initiate corrosion is due to the ability of Cr to form an adhesive and insoluble film, acting as a shield for the metal substrate [17].

The surface topography of the parts is marked by the method used at this level: mechanical processing (PM), sandblasting (S), oxidation by heat treatment (TTO), mechanical polishing (LM), or electrochemical (LE). Each of these surface conditioning processes influences the corrosion resistance of the part [18].

There are various methods of processing alloys for the manufacture of prosthetic structural components. Thus, the classic and established method of melting and casting alloy ingots in a refractory form obtained by melting the construction wax [19] can be mentioned.

The accessibility of the melting and casting processing method provides these materials with a wide range of uses. The durability of prosthetic frameworks not only represents the ability of the material to retain its properties in the functional context, but also the ability of the environment in which they were designed to be used as resistance prosthetic frameworks [20] and as supports for aesthetic ceramic components that can be built on as the alloy–ceramic system in which chemical adhesion (after sintering) of the ceramic layer on the metal component is very important [21].

This manufacturing method influences the mechanical properties of the alloy and its microstructure after the fabrication of the framework [5].

3. Structure of Co–Cr Alloys

Co–Cr–Mo alloys cast by the conventional method are composed of two phases (phase ɣ, with a cubic structure with centred faces, and phase ε, with a hexagonal structure), being stable at both high and low temperatures. In order to improve the mechanical properties of Co–Cr–Mo alloys, heat treatments can be applied to the manufactured frameworks.

Applying a heat treatment at a high temperature of about 1100 °C can determine a good homogenization of the cast structure of dental cobalt alloys. Additionally, the dendrites become finer [22]. Following the heat treatment, the volume proportion of the two phases can vary, producing a homogeneous structure with improved mechanical properties [5][23][24][25].

Co–Cr–W as-cast alloys have a balanced biphasic structure ɣ + ε due to their composition, which differs proportionally from the two phases of Co–Cr–Mo alloys, whose random atomic arrangement has commonly happened in the as-cast product. This will always be a discussion. Studies have shown that, for the homogenization thermal treatment process, there is a transformation from a random (disordered) to a more ordered structure. The solution treatment method can also produce ɣ-Co phase (FCC) followed by the hexagonal structure as a minor phase [26].

The as-cast specimens only exhibit diffraction peaks assigned to the ɣ phase. In contrast, both c and e reflections are observed for the heat-treated specimens. Thus, the e phase forms as a result of an athermal martensitic transformation that occurs during cooling after the heat treatment [26][27].

The presence of the gamma phase can be induced in another way: by reaching the temperature at which phase ε exits in the stability zone, isothermally, by reaching a temperature between 650–950 °C as a result of bending the deformation favouring the martensitic transformation of the alloy [27].

Depending on the nature and chemical composition of the samples, the morphology is different. The microstructure of Co–Cr dental alloys depends on the manufacturing technique. Given the differences in microstructural properties among the tested specimens, further differences in their technological achievement and clinical behavior can be anticipated [28].

4. Oxidation of Co–Cr Alloys

Oxidation at the surface of prosthetic framework by heat treatment is a method used to improve the bonds between Co–Cr alloys and plating ceramics, resulting in a physiognomic prosthetic reconstruction [29].

In order to create an optimal layer of oxides but also to achieve an efficient decontamination on the surface of the structure, the temperature of the oxidative heat treatment (OTT) must be between 960 °C and 980 °C, in accordance with the instructions of the alloy manufacturer [30].

The characteristics of the oxide layer to be considered are: color, thickness, and adhesion to the alloy that produced it. The finishing processes of the metal part, such as sandblasting, acid etching, and hardening agents, influence the connection between the alloy and the cladding ceramics [31].

Mo reduces the intensity of the oxidation phenomenon, ensuring the passivation and decrease in the tendency of breaking of the passive film [32].

The oxide layers on the surface of Co–Cr–W alloys are structured as follows: an outer layer of CoO, an intermediate layer rich in Cr, and a deep layer rich in W. The rapid oxidation of Co–Cr–W alloys at high temperatures results in the formation of W oxide, which makes the oxide layer much more adherent and resistant [33].

Oxidation is a self-protection ability of the material that is active from the design stage. The oxide layers on the surface of Co–Cr base alloys can be considered as an elastic buffer [34].

References

1. Uriciuc, W.A. Research about Precision Casting of Removable-Fixed Ensemble Applied in Dental Prosthodontics. In International Conference on Advancements of Medicine and Health Care through Technology; Springer: Berlin/Heidelberg, Germany, 2009; pp. 379–382.
2. Iulian, A.; Cosmin, S.; Aurora, A. Adhesion aspects in biomaterials and medical devices. J. Adhes. Sci. Technol. 2016, 30, 1–5.
3. Arnold, C.; Hey, J.; Schweyen, R.; Setz, J.M. Accuracy of CAD-CAM-fabricated removable partial dentures. J. Prosthet. Dent. 2018, 119, 586–592.
4. Niculescu, M.; Laptoiu, D.; Miculescu, F.; Antoniac, I.V. Metal Allergy and other Adverse Reactions in Patients with Total Hip Replacement. Adv. Mater. Res. 2015, 1114, 283–287.
5. Kim, H.R.; Jang, S.-H.; Kim, Y.K.; Son, J.S.; Min, B.K.; Kim, K.-H.; Kwon, T.-Y. Microstructures and Mechanical Properties of Co-Cr Dental Alloys Fabricated by Three CAD/CAM-Based Processing Techniques. Materials 2016, 9, 596.
6. Uriciuc, W.A.; Boșca, A.B.; Babtan, A.M.; Feurden, C.N.; Ionel, A.; Vermeșan, H.; Popa, C.O.; Ilea, A. Optimization of the Manufacturing Process by Molding Cobalt-Chrome Alloys in Assembled Dental Frameworks. Prosthesis 2021, 3, 245–260.

7. Uriciuc, W.A.; Vermesan, H.; Tiuc, A.E.; Ilea, A.; Bosca, A.B.; Popa, C.O. Casting over Metal Method Used in Manufacturing Hybrid Cobalt-Chromium Dental Prosthetic Frameworks Assembles. Materials 2021, 14, 539.
8. Petrut, A.; Ivanov, A.; Antoniac, I.; Miculescu, F.; Cosmeleata, G. Experimental researches about technological and microstructural aspects in the case of cobalt-chromium dental alloys. Eur. Cells Mater. 2007, 13, 28.
9. Uriciuc, W.A.; Vermeșan, H.; Boșca, A.B.; Ilea, A. Interaction of Saliva with Cobalt-Chromium-Based Dental Alloys in Casted Prosthetic Pieces. Curr. Trends Biomedical. Eng. Biosci. 2018, 14, 555882.
10. Upadhyay, D.; Panchal, M.A.; Dubey, R.S.; Srivastava, V.K. Corrosion of alloys used in dentistry: A review. Mater. Sci. Eng. A 2006, 432, 1–11.
11. Wataha, J.C.; Schmalz, G. Dental Alloys. In Biocompatibility of Dental Materials; Springer: Berlin/Heidelberg, Germany, 2009; pp. 221–254.
12. Kassapidou, M.; Franke Stenport, V.; Hjalmarsson, L.; Johansson, C.B. Cobalt-chromium alloys in fixed prosthodontics in Sweden. Acta Biomater. Odontol. Scand. 2017, 3, 53–62.
13. Lucchetti, M.C.; Fratto, G.; Valeriani, F.; De Vittori, E.; Giampaoli, S.; Papetti, P.; Spica, V.R.; Manzon, L. Cobalt-chromium alloys in dentistry: An evaluation of metal ion release. J. Prosthet. Dent. 2015, 114, 602–608.
14. Puskar, T.; Jevremovic, D.; Williams, R.J.; Eggbeer, D.; Vukelic, D.; Budak, I. A Comparative Analysis of the Corrosive Effect of Artificial Saliva of Variable pH on DMLS and Cast Co-Cr-Mo Dental Alloy. Materials 2014, 7, 6486–6501.
15. Hsu, R.W.-W.; Yang, C.-C.; Huang, C.-A.; Chen, Y.-S. Electrochemical corrosion studies on Co–Cr–Mo implant alloy in biological solutions. Mater. Chem. Phys. 2005, 93, 531–538.
16. Lee, S.-H.; Takahashi, E.; Nomura, N.; Chiba, A. Effect of Carbon Addition on Microstructure and Mechanical Properties of a Wrought Co–Cr–Mo Implant Alloy. Mater. Trans. 2006, 47, 287–290.
17. Alifui-Segbaya, F.; Foley, P.; Williams, R.J. The corrosive effects of artificial saliva on cast and rapid manufacture-produced cobalt chromium alloys. Rapid Prototyp. J. 2013, 19, 95–99.
18. Surmann, H.; Huser, J. Automatic electropolishing of cobalt chromium dental cast alloys with a fuzzy logic controller. J. Comput. Chem. Eng. 1998, 22, 1099–1111.
19. Reimann, L.; Dobrzański, L.A. Influence of the casting temperature on dental Co-base alloys properties. Arch. Mater. Sci. Eng. 2013, 60, 5–12.
20. O’Brien, J.O. Dental Materials and Their Selection, 3rd ed.; Quintessence Publishing Co, Inc.: Hanover Park, IL, USA, 2002; ISBN 0-86715-406-3.

21. Miculescu, M.; Bane, M.; Miculescu, F.; Ciocan, L.T.; Preda, O.; Antoniac, I.V. A Study on Metal-Ceramic Interface on Metal Base Dental Alloys. Key Eng. Mater. 2015, 638, 14–19.
22. Ghiban, A.; Ghiban, B.; Borţun, C.M.; Ghiban, N.; Antoniac, I.V. Heat Treatments Influence on Corrosion Resistance of some New Dental Cobalt Alloys. Solid State Phenom. 2012, 188, 93–97.
23. Saldıvar, A.; López, H. Role of aging on the martensitic transformation in a cast cobalt alloy. Scr. Mater. 2001, 45, 427–433.
24. Lashgari, H.R.; Zangeneh, S.; Hasanabadi, F.; Saghafi, M. Microstructural evolution during isothermal aging and strain-induced transformation followed by isothermal aging in Co-Cr-Mo-C alloy: A comparative study. Mater. Sci. Eng. A 2010, 527, 4082–4091.
25. Mori, M.; Yamanaka, K.; Chiba, A. Phase decomposition in biomedical Co–29Cr–6Mo–0.2N alloy during isothermal heat treatment at 1073K. J. Alloy. Compd. 2014, 590, 411–416.
26. Lu, Y.; Wu, S.; Gan, Y.; Zhang, S.; Guo, S.; Lin, J.; Lin, J. Microstructure, mechanical property and metal release of As-SLM CoCrW alloy under different solution treatment conditions. J. Mech. Behav. Biomed. Mater. 2016, 55, 179–190.
27. Huang, P.; López, H. Strain induced ε-martensite in a Co–Cr–Mo alloy: Grain size effects. Mater. Lett. 1999, 39, 244–248.
28. Savencu, C.E.; Porojan, L.; Bîrdeanu, M.; Boloș, A.; Porojan, S.; Antoniac, A.; Gradinaru, S. Surface Characteristics of Base Metal Dental Alloys Processed by Alternative Procedures. In Defect and Diffusion Forum; Trans Tech Publications Ltd: Geneva, Switzerland, 2017; Volume 376, pp. 1–11.
29. Wu, Y.; Moser, J.; Jameson, L.; Malone, W. The effect of oxidation heat treatment on porcelain bond strength in selected base metal alloys. J. Prosthet. Dent. 1991, 66, 439–444.
30. Dent, R.J.; Preston, J.D.; Moffa, J.P.; Caputo, A. Effect of oxidation on ceramometal bond strength. J. Prosthet. Dent. 1982, 47, 59–62.
31. Jones, D.W. Coatings of Ceramics on Metals. Ann. N. Y. Acad. Sci. 1988, 523, 19–37.
32. Park, S.-J.; Seo, S.-M.; Yoo, Y.-S.; Jeong, H.-W.; Jang, H. Effects of Cr, W, and Mo on the High Temperature Oxidation of Ni-Based Superalloys. Materials 2019, 12, 2934.
33. Park, W.U.; Park, H.G.; Hwang, K.H.; Zhao, J.; Lee, J.K. Interfacial Property of Dental Cobalt–Chromium Alloysand Their Bonding Strength with Porcelains. J. Nanosci. Nanotechnol. 2017, 17, 2585–2588.
34. Uriciuc, W.A.; Vermeşan, H.; Botean, A.I.; Nistor, L.; Catalin, P.O.P.A. Research on the surface of the dental alloys with cobalt-crom base. Acta Tech. Napoc.-Ser. Appl. Math. Mech. Eng. 2019, 62. Available online: https://atna-mam.utcluj.ro/index.php/Acta/article/view/1244 (accessed on 13 March 2022).