

TRIBO-CORROSION BEHAVIOR OF CAST AND SELECTIVE LASER MELTED Co-Cr ALLOY FOR DENTAL APPLICATIONS

Assist. Prof. Ş. Hakan Atapek¹, Assoc. Prof. Tsanka Dikova^{2*}, MSc. Gülşah Aktaş¹,
Assoc. Prof. Şeyda Polat¹, Assist. Prof. Dzhendo Dzhendov², Diana Pavlova³,
Assist. Prof. Maksim Simov³

¹Faculty of Engineering, Department of Metallurgical and Materials Engineering, Kocaeli University, 41380, Kocaeli, Turkey

²Faculty of Dental Medicine, Medical University of Varna, 55 Marin Drinov Str, 9000 Varna, Bulgaria

³Medical College, Medical University of Varna, 55 Marin Drinov Str, 9000 Varna, Bulgaria

* tsanka_dikova@abv.bg

Abstract: Cobalt-chromium based alloys are widely used in dental applications due to their excellent mechanical properties, high corrosion resistance and good biocompatibility. Although they are generally fabricated by casting for dental restorations, recently selective laser melting (SLM) has become an attractive production method since it allows complex geometries. Recent studies revealed that Co-Cr alloys formed by SLM, provided better corrosion resistance as well.

In this study, tribo-corrosion behavior of a Co-Cr-Mo alloy produced by casting (Biosil-Degudent) was compared with the one (Co212-f ASTM F75) produced by SLM. The wear properties were investigated by tribo-corrosion tests in a Fusayama-Meyer artificial saliva solution using a "ball-on-disc" type tribometer. Polished surfaces were tested against zirconia balls at the same sliding speed, distance and load. Friction coefficient values were determined and the worn surfaces were evaluated using microscopes to compare the wear and tribo-corrosion resistance through wear tracks. SLM proved to be a promising manufacturing method for dental applications.

Keywords: DENTAL Co-Cr ALLOYS, CASTING, SELECTIVE LASER MELTING, TRIBO-CORROSION

1. Introduction

Due to a great demand in artificial hip, knee joints and dental applications, many attempts were made to produce materials having superior physical and chemical properties [1]. Co-Cr-Mo alloys are commonly used as implant materials as well as restoration materials in dentistry due to their excellent mechanical properties, high corrosion resistance and good biocompatibility [2]. They possess face centered cubic (FCC) lattice - γ phase at high temperatures and hexagonal close packed (HCP) lattice - ϵ phase at room temperature [3-6]. While γ phase is responsible for ductility, ϵ phase enhances the corrosion and wear resistance [7]. In proper alloying the microstructure of the dental alloys is composed mainly of γ phase and carbides of the $M_{23}C_6$ type [4]. Chromium, molybdenum and tungsten are added for strengthening of the solid solution. The chromium (22%-28%) forms a passive oxide layer on the surface providing good corrosion resistance and carbides in the microstructure increase the hardness and wear resistance [4, 6]. Consecutively, the properties of the dental alloys depend on the γ - ϵ ratio and the type, quantity and distribution of the carbide phase in the microstructure.

Not only grade of material but also processing technique have an important role on the final properties of implant materials [8]. From past to present, casting is a well-known technique to produce several metallic products, however, cast alloys having inhomogeneous microstructure, solidification defects, segregation and large grains are not sufficient to ensure high quality, superior physical and chemical properties leading to a long service life [9]. Today, selective laser melting (SLM) technique, a kind of additive manufacturing method, is preferred in fabricating implant materials due to its highly motivated facilities [10]. In this technology layers of metal powder are fused into a 3D model by adopting a computer-directed laser [11-13]. The advantages of SLM over the traditional methods include production of personalized complex objects; manufacturing of parts with dense structure and predetermined surface roughness; controllable, easy and relatively quick process [11]. The SLM process is characterized by high heating and cooling rates of the melted layer as well as heating and solid state phase transformations in the underneath layers, which determine microstructure and properties quite different than that of the cast details.

It was established by Meacock et al. [14] that the microstructure of biomedical Co-Cr-Mo alloy, produced by laser powder microdeposition, is homogenous comprised of fine cellular

dendrites. The average hardness was 460 HV0.2, which is higher than the values obtained by the other fabrication processes. Barucca *et al.* [15] investigated Co-Cr-Mo parts, produced by direct metal laser sintering. They established that the higher hardness is attributed to the presence of the ϵ -lamellae grown on the $\{111\}\gamma$ plane. Dolgov *et al.* [16] also reported about more homogeneous microstructure, the higher hardness and yield strength of the SLM fabricated Co-Cr-Mo alloy (382 HV and $R_{0.2}=720$ MPa) comparing to the cast alloy (335 HV and $R_{0.2}=410$ MPa). Lu *et al.* [17] investigated the microstructure, hardness, mechanical properties, electrochemical behavior and metal release of Co-Cr-W alloy fabricated by SLM in two different scanning strategies – line and island. They established the coexistence of the γ - and ϵ -phases in the microstructure and nearly the same hardness (570 HV for line-formed alloy and 564 HV for island-formed) as well as high corrosion resistance in the both production schemes. The higher hardness and the more homogeneous microstructure of SLM Co-Cr alloys are preconditions for higher wear and corrosion resistance, respectively.

Tribo-corrosion is a relatively new field of physical science research in which two degradation processes, mechanical wear and electrochemical responses to particular consequences of that wear, are studied [18]. In general, the tribo-corrosion behavior of metals can be attributed to the synergy between wear and corrosion and the leading phenomena can be summarized as the following: (i) an oxide film forms on the metal surface and it protects the surface from corrosion degradation, (ii) wear removes the film inducing an accelerated corrosion process, (iii) wear-corrosion products enhance the wear, (iv) the synergy between wear and corrosion exponentially causes a great material loss. This synergy can be varied by not only test conditions (corrosive medium, temperature, tribological pairs, load, sliding speed etc.) but also microstructural features [19]. In this study, cast and SLM processed two commercial alloys were tested in artificial saliva solution to understand their tribo-corrosion behavior throughout the microstructural features.

2. Materials and methods

Materials and sample preparation

In this study, two commercial Co-Cr-Mo alloys (Biosil-Degudent and Co212-f ASTM F75) were selected as test materials. Biosil-Degudent alloy was produced by casting and its composition includes 64.80 Co - 28.50 Cr - 5.30 Mo - 0.50 Si - 0.50 Mn - 0.40 C,

wt-%. It has a hardness value of 400 HV10 and its yield strength and tensile strength are 700 MPa and 900 MPa, respectively. The chemical composition of SLM processed Co212-f ASTM F75 alloy contains 65.20 Co - 28.30 Cr - 5.48 Mo - 0.754 Si - 0.164 Fe - 0.036 V, wt-%. Its hardness value is 35 HRC and yield and tensile strength values are 835 MPa and 1050 MPa, respectively. All data about the chemical composition and also mechanical properties are provided by the manufacturer.

Test specimens with dimensions 2 mm x 10 mm x 40 mm were prepared by lost-wax casting and SLM process. At first a silicone mold for manufacturing of wax models for the cast test specimens was fabricated, while the 3D model was created with SolidWorks software. The cast samples were produced by centrifugal casting of Co-Cr alloy "Biosil". The SLM samples were fabricated directly from the virtual 3D models using SLM 125 machine of the "SLM Solutions", Germany. The machine is equipped with continuous Nd:YAG laser which worked with power 100 W and laser spot diameter 0.2 mm. The metal powder of Co-Cr alloy Co212-f ASTM F75 was melted in layers with 0.03 mm thickness until the desired construction was obtained. During manufacturing process the laser at first scanned the outer contour of the layer of the first specimen's part, next it hatched the area within the boundaries at an angle of 45° with a pitch of 0.13 mm. After that it passed to the same layer of the next specimen's part, thus fabricating the whole layer. The SLM technological regime, recommended from the company producer was used.

Sample characterization

Samples were cold molded and surfaces were prepared by standard metallographical techniques, namely grinding with SiC papers, polishing with diamond paste. Surfaces were etched electrolytically in a solution (5 % HCl, 95 % H₂O), at 5 V for 1 sec. Microstructural characterization was carried out using light microscope (LM, Olympus BX41M-LED) and scanning electron microscope (SEM, Jeol JSM 6060) equipped with energy dispersive spectrometer (EDS, IXRF).

Tribo-corrosion test

For tribological studies, a "ball-on-disc" type tribometer (Nanovea Microtest SMT/A) was used and the system was supported by a home-made attachment for the tribo-corrosion tests. In this system (Fig. 1), molded alloys having equal contact areas were fixed into a polymeric chamber and polished surfaces were subjected to a Fusayama-Meyer artificial saliva solution (pH ~ 7.1). The counterpart material was selected as ZrO₂ having 3 mm diameter and the tests were carried out under 5N normal load, at a speed of 0.01 m/s during 100 m for 3 ½ h.

All test results were evaluated by (i) variation of friction coefficient (COF) as a function of sliding distance, (ii) determination the change in weight, (iii) worn surface examinations by SEM. Weight loss values for all samples were determined by weighing the specimens before and after the tests using a precise laboratory type balance.

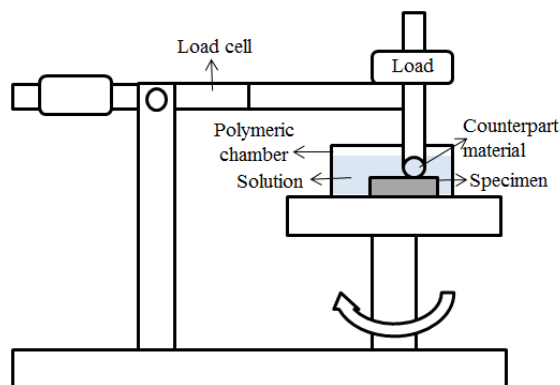


Fig. 1: A schematic illustration of a "ball-on-disc" type tribometer equipped with tribo-corrosion unit.

3. Results and discussion

Fig. 2a shows a typical cast structure of Co-Cr-Mo alloy and it consists of γ -Co dendritic matrix of face centered cubic structure and a secondary blocky $M_{23}C_6$ carbide phase segregated to the columnar grained structure (Fig. 2b). As reported in several studies [4, 16, 20-22], the cast matrix includes large grains, non-homogenous microstructure, solidification defects resulting in poor mechanical properties. The coarse grain structure will be very effective on the chipping failure thus the material used in dental applications should consist of smaller grains [17]. This problem could be overcome by SLM which is an additive manufacturing technique, fabricating metal products having very fine and well distributed microstructural features within matrix [14-17, 20]. In SLM processed materials, laser scan produces a layer-layer molten pool boundaries (MPBs) given in Fig. 3a and SEM observations at higher magnification revealed out the presence of an extremely fine microstructure inside a single pool (Fig. 3b) and very fine carbides having globular (drawn by circle) and lamellar (drawn by square) morphology are observed in re-solidified structure (Fig. 4).

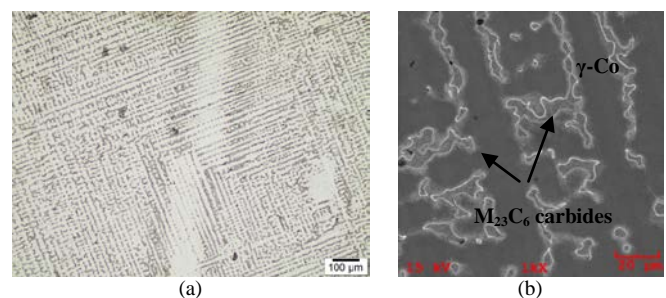


Fig. 2: Microstructures of cast Co-Cr-Mo alloy: (a) LM image showing typical cast structure γ -Co dendritic matrix, (b) SEM image showing secondary $M_{23}C_6$ carbides at the boundaries.

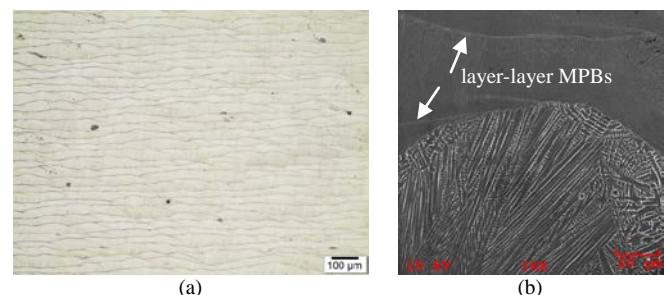


Fig. 3: Microstructures of SLM processed Co-Cr-Mo alloy: (a) LM image showing layer-layer MPBs, (b) SEM image revealing out the finer structure compared to cast alloy.

Fig. 5 shows the variation of COF as a function of sliding distance for tested alloys. The curves include typical fluctuations due to ploughing and adhesion of moving particles formed by wear and corrosion and they consist of two distinct regimes: (i) running-in regime at first 10 m and (ii) steady-state regime after 25 m. Till the end of running-in regime, the cast alloy has a tendency to increase its COF value and it has a peak value of 0.09, however, COF value of SLM alloy initially has its maximum value as 0.13 and then goes down during sliding. At the steady-stage regime, the COF values of both alloys have no significant change and vary in the range of 0.08 - 0.10. Studied alloys owe their wear resistance to the hard carbides (especially Cr-rich carbides) within their matrix, however, these carbides have a detrimental effect in corrosive medium due to depletion of chromium away from the matrix and lack of protective film [predominantly Cr₂O₃ and Cr(OH)₃] on the metal surface [23]. This detrimental effect can be observed as pits and crevices in the surrounding areas of the carbide due to localized attack in corrosive medium. In sliding of tribological pairs in a corrosive medium, the corrosion resistant carbides stick out and behave as asperities deteriorating the protective film, grooving the surface, leading to corrosion products and increasing the COF [6]. All these well-known approaches make it clear why the cast alloy having coarser microstructural features (columnar structure and

blocky carbides) than that of SLM processed alloy exhibited a rapid COF increase in running-in regime. On the other hand, SLM processed alloy keeps its chromium in the matrix, therefore, more stable oxide layer makes the alloy resistant to both corrosion and wear despite a normal force is subjected to tested alloy embedded into a corrosive medium and corrosion potential shifts from a passive region to a more active region due to frictional forces.

As mentioned before, the synergy between wear and corrosion causes a great material loss forming an adhesion layer. The presence of adhesion layer may change the tribological interaction from two-body contact to three-body contact at the steady-state regime in which both cast and SLM alloys exhibit similar COF values. Not only variation of COF values but also changes in weight support the effect of microstructural features of Co-Cr-Mo alloys on tribo-corrosion behavior. When the weights of the alloys before and after the tribo-corrosion test were considered, a gain of 3.3 mg and 1.8 mg were observed for the cast and SLM alloys, respectively. The increase is mainly due to the corrosion products accumulated on the worn surfaces together with the wear debris, and it is almost twice as much for the cast alloy compared to the SLM one clearly indicating that it suffered more from corrosion and wear under the given conditions.

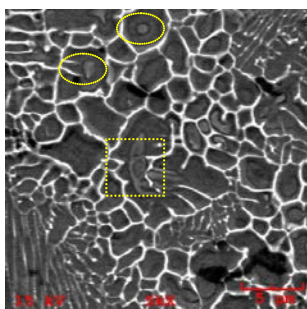


Fig. 4: SEM image showing globular and lamellar shaped carbides in columnar structure of SLM processed alloy.

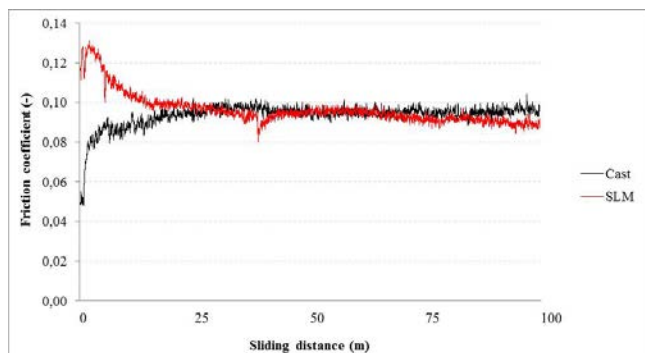


Fig. 5: Variation of COF values as a function of sliding distance.

The worn surfaces of studied alloys were also examined by SEM and Fig. 6 shows the general views of wear tracks formed on the surfaces. Worn surface of cast alloy exhibited a very smooth wear track and a thick degraded film layer compared to that of SLM processed alloy. The film layer formed on cast alloy consists of 21.32 O - 0.20 Na - 0.70 Si - 6.90 P - 0.01 Cl - 4.32 Ca - 18.30 Cr - 10.36 Fe - 5.20 Mo - 32.69 Co (wt-%) and the elemental distribution indicates that (i) the degraded film includes not only passive layer of Cr-Co-Mo oxides like Cr_2O_3 , CoO and MoO_3 but also Fe and Si based oxides due to depletion of Fe and Si ions having more negative standard reduction potential close to that of Cr, (ii) the presence of Cl and Na is a good evidence for the formation of chloride salts, (iii) the presence of phosphorus and calcium is related with the formation of a phosphate and carbonate compounds as reported in previous studies [23]. The film layer of SLM processed alloy has also similar elemental distribution (25.55 O - 0.43 Na - 0.63 Si - 6.45 P - 0.04 Cl - 3.00 Ca - 20.70 Cr - 8.42 Fe - 4.35 Mo - 30.43 Co, wt-%) on its corroded surface.

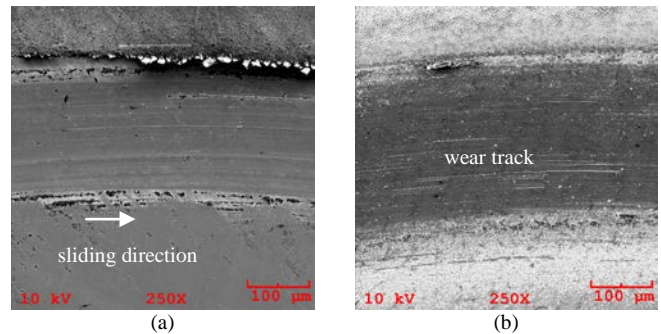


Fig. 6: SEM images showing a general view of worn surfaces: (a) cast and (b) SLM processed alloy.

SEM image given in Fig. 7 shows the pittings and cracks on the worn surface of cast alloy. In sliding conditions, the removed particles can be cold welded and then layered due to adhesive forces and then adhered layer can be deteriorated by delamination during contact. In this case, the detached particles will be very effective in wear and form new surfaces for the friction within the frame of three-body contact. Meanwhile, pitting corrosion is involved as point or small hole on the surface of metal embedded into a corrosive medium and pits can initiate at surface defects. A rapid depletion of oxygen in the pits causes metal oxidation and a progressive damage consisting of crack initiation and propagation into the porous and brittle oxide film starts [24, 25].

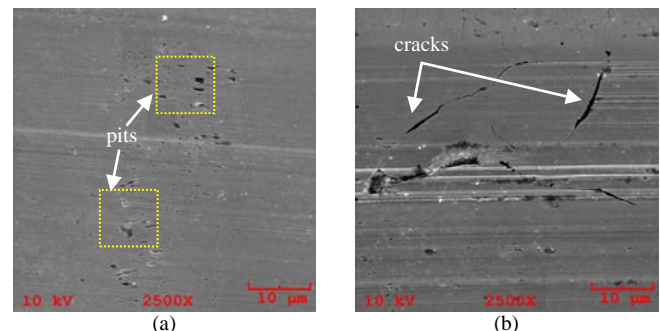


Fig. 7: SEM images showing several pits (a) and (b) cracking in adhered layer on the worn surface of tested cast alloy.

The worn surfaces given in Fig. 8 exhibited very different surface characteristics compared to cast alloy. The surface has very sharp plastic flows which are oriented step by step due to layer-layer structure of SLM processed alloy and also deep grooves indicating abrasion type wear. As examined before, SLM processed alloy has a finer microstructure compared to cast alloy and this structure makes it harder by plastic deformation during the contact of a harder counterpart. A decrease in the hardness gradient between tribological pairs increase the scratch capability of any surface and the abrasion wear appears.

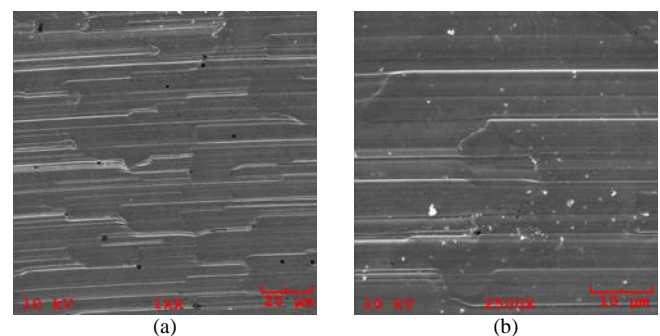


Fig. 8: SEM images showing plastic flows on the worn surface of SLM processed alloy: (a) plastic flows which are oriented step by step due to layer-layer structure of tested alloy, (b) deep grooves indicating the abrasion type wear under studied conditions.

4. Conclusions

The wear properties of Co-Cr-Mo alloys, fabricated by casting and SLM, were investigated by tribo-corrosion tests in a Fusayama-Meyer artificial saliva solution. As a result of different production processes, the microstructures of the cast and SLM samples differ considerably, thus revealing different wear and corrosion properties.

The friction coefficient (COF) of the cast alloy has a tendency to increase till the end of the running-in regime and it has a peak value of 0.09. COF value of SLM alloy initially has its maximum value as 0.13 and then goes down during sliding. At the steady-state regime, the COF values of both alloys have no significant change and vary in the range of 0.08 – 0.10.

The examination of the worn surfaces reveals different wear types for the cast and SLM Co-Cr-Mo alloys. The worn surface of the cast alloy exhibits a very smooth wear track with many pits and cracks as well as a thick degraded film layer. While the worn surface of the SLM alloy has very sharp plastic flows which are oriented step by step due to the alloy's layer-layer structure and also deep grooves exist indicating abrasion type wear.

Due to the more homogeneous microstructure, the higher hardness and the more stable oxide layer formed on the surface, the SLM processed alloy is more resistant to both corrosion and wear, thus proving that the SLM is a promising manufacturing method for dental applications.

5. References

- [1] B. D. Ratner, A. S. Hoffman, F. J. Schoen, J. E. Lemons (Eds.), "Biomaterials science", 3rd edition, Elsevier, 2013.
- [2] N. Rinčić, I. Baučić, S. Miko, M. Papić, E. Prohić, "Corrosion behaviour of the Co-Cr-Mo dental alloy in solutions of different composition and different pH values", *International Journal Collegium Antropologicum*, 27(2), 99-106, 2003.
- [3] K. P. Gupta, "The Co-Cr-Mo (Cobalt-Chromium-Molybdenum) System", *Journal of Phase Equilibria and Diffusion* 26 (1), 87-92, 2005.
- [4] M. Podrrez-Radziszewska, K. Haimann, W. Dudzinski, M. Morawska-Soltysik, "Characteristic of intermetallic phases in cast dental CoCrMo alloy", *Archives of Foundry Engineering* 10(3), 51-59, 2010.
- [5] P. Crook, "Metals handbook - nonferrous alloys and special-purpose materials", ASM International, Materials Park, Ohio-USA, 1990.
- [6] G. Bellefontaine, "The corrosion of CoCrMo alloys for biomedical applications", MSc thesis, School of Metallurgy and Materials, University of Birmingham, January 2010.
- [7] S. Kurosu, N. Nomura, A. Chiba, "Effect of sigma phase in Co-29Cr-6Mo alloy on corrosion behavior in saline solution", *Materials Transactions*, 47(8), 1961-1964, 2006.
- [8] L. Hao, J. Lawrence, "Laser surface treatment of bio-implant materials", John Wiley and Sons, 2005.
- [9] M. P. Groover, "Fundamentals of modern manufacturing – materials, processes and systems", 4th edition, John Wiley and Sons, 2010.
- [10] S. L. Campanelli, N. Contuzzi, A. Angelastro, A. D. Ludovico, N. Contuzzi, "Capabilities and performance of the selective laser melting process", Intech Open Access Publisher, 2010.
- [11] K. Torabi, E. Farjood, Sh. Hamedani, "Rapid prototyping technologies and their applications in prosthodontics- a review of literature", *Journal of Dentistry - Shiraz Univ. Med. Sci.*, 16(1), 1-9, 2015.
- [12] K. Quante, K. Ludwig, M. Kern, "Marginal and internal fit of metal-ceramic crowns fabricated with a new laser melting technology", *Dental Materials*, 24, 1311-1315, 2008.
- [13] Y. Ucar, T. Akova, M. S. Akyil, W. A., Brantley, "Internal fit evaluation of crowns prepared using a new dental crown fabrication technique: laser-sintered Co-Cr crowns", *The Journal of Prosthetic Dentistry*, 102, 253-259, 2009.
- [14] C. G. Meacock, R. Vilar, "Structure and properties of a biomedical Co-Cr-Mo alloy produced by laser powder microdeposition", *Journal of Laser Applications*, 21, 88-95, 2009.
- [15] G. Barucca, E. Santecchia, G. Majni, E. Girardin, E. Bassoli, L. Denti, A. Gatto, L. Iuliano, T. Moskalewicz, P. Mengucci, "Structural characterization of biomedical Co-Cr-Mo components produced by direct metal laser sintering", *Materials Science and Engineering C*, 48, 263-269, 2015.
- [16] N. A. Dolgov, T. Dikova, D. Dzhendov, D. Pavlova D., M. Simov, "Mechanical properties of dental Co-Cr alloys fabricated via casting and selective laser melting", *International Journal Materials Science Non-Equilibrium Phase Transformations*, 3, 7-11, 2016.
- [17] Y. Lu, S. Wu, Y. Gan, J. Li, C. Zhao, D. Zhuo, J. Lin, "Investigation on the microstructure, mechanical property and corrosion behavior of the selective laser melted CoCrW alloy for dental application", *Materials Science and Engineering C*, 49, 517-525, 2015.
- [18] M. Mathew, S. Kerwell, M. Alfaro, D. Royman, V. Barao, S. Cortino, "Tribocorrosion and TMJ TJR devices", in L.G. Mercuri (ed.), *Temporomandibular joint total joint replacement – TMJ TJR, A Comprehensive Reference for Researchers, Materials Scientists, and Surgeons, Part IV*, Springer, 251-263, 2016.
- [19] D. Landolt, S. Mischler (Eds.), "Tribocorrosion of passive metals and coatings", 1st edition, Woodhead Publishing, 2011.
- [20] T. Dikova, D. Dzhendov, M. Simov, "Microstructure and hardness of fixed dental prostheses manufactured by additive technologies", *Journal of Achievements in Mechanical and Materials Engineering*, 71(2), 60-69, 2015.
- [21] I. S. Braude, N. N. Galtsov, A. I. Prokhvatilov, E. N. Chaika, "Phase composition of cast Ni-Cr-Mo and Co-Cr-Mo alloys", *The Physics of Metals and Metallography*, 100(2), 165-171, 2005.
- [22] H. Herø, "Effects of casting temperature on some properties of Co-Cr-Mo dental casting alloys", *Acta Odontologica Scandinavica*, 42(6), 371-377, 1984.
- [23] R. A. Rodriguez-Diaz, A. L. Ramirez-Ledesma, M. A. Aguilar-Mendez, J. U. Chavarin, M. A. H. Gallegos, J. A. Juarez-Islas, "Electrochemical corrosion behavior of a Co20Cr alloy in artificial saliva", *International Journal of Electrochemical Science*, 10, 7212-7226, 2015.
- [24] İ. Ünal, S. Zor, H. Atapek, "Influence of artificial saliva on NiTi orthodontic wires : a study on the surface characterization", *Materials Science*, 47(6), 830-837, 2012.
- [25] H. İ. Ünal, "Effect of fluoride added artificial saliva solution on orthodontic wires", *Protection of Metals and Physical Chemistry of Surfaces*, 48(3), 367-370, 2012.