Volume 71 • Issue 2 • August 2015

Journal of Achievements in Materials and Manufacturing Engineering

International Scientific Journal published monthly by the World Academy of Materials and Manufacturing Engineering

Microstructure and hardness of fixed dental prostheses manufactured by additive technologies

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ABSTRACT

Purpose: The additive technologies characterize with building of one layer at a time from a powder or liquid that is bonded by means of melting, fusing or polymerization. The methods, mostly used in dentistry, include selective laser sintering, selective laser melting and 3D printing. The aim of the present paper is to investigate the microstructure and hardness of fixed dental prostheses produced by three different technologies.

Design/methodology/approach: Four-part dental bridges were manufactured of Co-Cr alloy by standard lost-wax process, casting of 3D printed wax models and Selective Laser Melting (SLM). The microstructure was investigated by optical microscopy and SEM. EDX and EPMA analyses and Vickers microhardness measurements was done.

Findings: It was established that the microstructure of cast samples is dense, inhomogeneous, consisting of large grains with dendrite morphology, while the microstructure of the SLM bridges is porous. Pores, elongated along the direction of the melted layers were observed. The microhardness investigations showed highest average hardness of the samples, produced by SLM (356HV-407HV), followed by the hardness of the samples, cast by 3D printed models (327HV-343HV) and these, manufactured by standard lost-wax process (251HV-274HV). The measurements along depth of the samples showed nearly even microhardness distribution in the bridges, produced by SLM, and fluctuations of the microhardness values along the depth of the cast bridges due to the inhomogeneous microstructure.

Research limitations/implications: As the additive technologies for production of dental restorations from wax, polymers and metal alloys are developed last years, additional investigations are needed for development of more precise technological regimes.

Originality/value: The comparison between the microstructure and hardness of dental prostheses made by lost-wax process and SLM reveals the peculiarities of the constructions produced by new technology.

Keywords: Biomaterials; Additive Technologies; Fixed Dental Prostheses; Microstructure and Hardness

Reference to this paper should be given in the following way:

Ts. Dikova, Dzh. Dzhendov, M. Simov, Microstructure and hardness of fixed dental prostheses manufactured by additive technologies, Journal of Achievements in Materials and Manufacturing Engineering 71/2 (2015) 60-69.

PROPERTIES

1. Introduction

The fixed dental prosthesis is any dental prosthesis that is luted or mechanically attached to natural teeth, tooth roots, and/or dental implant abutments. This may include replacement of one to sixteen teeth in each dental arch [1]. The crown and bridges are fixed dental prostheses which restore damaged tooth or substitute one or two missing teeth. The dental bridge is held in place using two crowns bonded on adjacent teeth [2]. It is usually made of metal alloys, covered with polymer or composite, metal-ceramic or porcelain.

Co-Cr alloys are mostly used for manufacturing of metal framework of fixed dental prosthesis because of their high mechanical properties, high corrosion and wear resistance, high biocompatibility and comparatively low price. They possess face centred cubic (FCC) lattice - γ phase in high temperatures and hexagonal close packed (HCP) lattice - ε phase in room temperature [3-6]. The γ phase is responsible for ductility, while the 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 and carbides in the microstructure which increase the corrosion resistance and the hardness and wear resistance respectively [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.

The microstructure and properties of the metal framework depend on the manufacturing process and the technological regimes. Most of the dental constructions are cast by lost-wax process in which the wax model of the framework is manufactured manually, leading to low accuracy and satisfactory quality. In the late 1980s the new approach to the production of constructions appeared – by addition of material layer by layer. The additive technologies were developed, which characterize with building of one layer at a time from a powder or liquid that is bonded by means of melting, fusing or polymerization. They offer a number of advantages over the traditional methods: production of personalized complex objects without need of complex machinery; manufacturing of parts with dense structure and predetermined surface roughness; controllable, easy and relatively quick process [8-10]. The methods, mostly used in dentistry, include selective laser sintering, selective laser melting (SLM), stereolithography, fused deposition modeling and selective electron beam melting (SEBM). Gaytan et al. [11] established that the high hardness of Co-based prototypes, produced by SEBM, is due to the ordinate array of metal carbides. Meacock et al. [12] reported that the microstructure of biomedical Co-Cr-Mo alloy, produced by laser powder microdeposition, is homogeneous comprised of fine cellular dendrites. The average hardness was 460 HV0,2, which is higher than the values obtained by the other fabrication process. Barucca et al. [13] investigated Co-Cr-Mo parts, produced by direct metal laser sintering. They established that microstructure consists of γ and ε phases. The ε phase is formed by athermal martensitic transformation and it is distributed as network of thin lamellae inside the γ phase. The higher hardness is attributed to the presence of the ε-lamellae grown on the $\{111\}_\gamma$ planes that restricts the dislocations movement in the γ phase. Yanjin Lu et al. [14] investigated the microstructure, hardness, mechanical properties, electrochemical behaviour 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. Their research show that the results of tensile, hardness, density, electrochemical and metal release tests are independent of the scanning strategy and the yield strength of both samples meet the ISO 22764:2006 standard for dental restorations.

As all types of the additive technologies are new and the new technologies are developed very rapidly last years, there are only a few data about the accuracy, surface properties, microstructure and mechanical properties of the constructions manufactured by them. The aim of the present paper is to investigate the microstructure and hardness of fixed dental prostheses produced of Co-Cr alloy by three different technologies – lost-wax casting of standard wax model, lost-wax casting of 3D printed polymer model and selective laser melting.

2. Experimental methods

In order to obtain samples with sufficiently good repeatability at first a base model of 4-part dental bridge was made. It was used for manufacturing of silicone mold for production of wax models and for generating of virtual 3D model. 5 samples of dental bridges were manufactured by each of the three different technologies. The first technology was standard lost-wax process, in which the wax models were produced in silicone mold. After that the

bridges were cast by centrifugal casting of Co-Cr alloy „Biosil" with chemical composition, given by the producer: 64.8% Co; 28,5% Cr; 5.3% Mo; 0.5% Si; 0.5% Mn; 0.4% C (wt.%). During the second technological process the bridges were cast of the same alloy but the models were produced of polymer by 3D printing using „Solidscape 66+" system. To obtain maximal accuracy the thickness of the printed layers was 0,.0127 mm. In the third technology the bridges were produced directly from the virtual 3D model by selective laser melting using SLM125 machine of the "SLM Solutions" company, Germany. The base material - metal powder of Co-Cr alloy (Co212-f ASTM F75) with the same chemical composition as that of „Biosil" alloy was melted in layers with 0,03 mm thickness unless the desired construction was obtained. Technological regime, recommended by the manufacturer, was used.

The microstructure of the preliminary prepared cross-sections of the bridges was investigated by optical microscopy and dual beam scanning electron / focused ion beam system (SEM/FIB LYRA I XMU, TESCAN), equipped with EDX detector (Quantax 200, Bruker). EDX and EPMA analyses were done. The Vickers micro-hardness was measured along depth of all elements of the bridges with 100 gf loading.

3. Results obtained

3.1. Microstructure

The microstructure of the sample, cast by lost-wax process of wax model manufactured in silicone mold, consists of large grains with dendrite morphology (Fig.1a). A lot of carbides of irregular shape and large sizes can be seen along the grain boudaries. Small quantity of carbides of small sizes and round shape are observed inside the grains. The SEM observations reveal that the carbides are located in the interdendritic areas (Fig.1b) and the interdendritic regions consist of eutectic with small round shape carbides in it (Fig.1c). The back scattered electron image on Fig.1d presents the precipitation of large carbides in the interdendritic space.

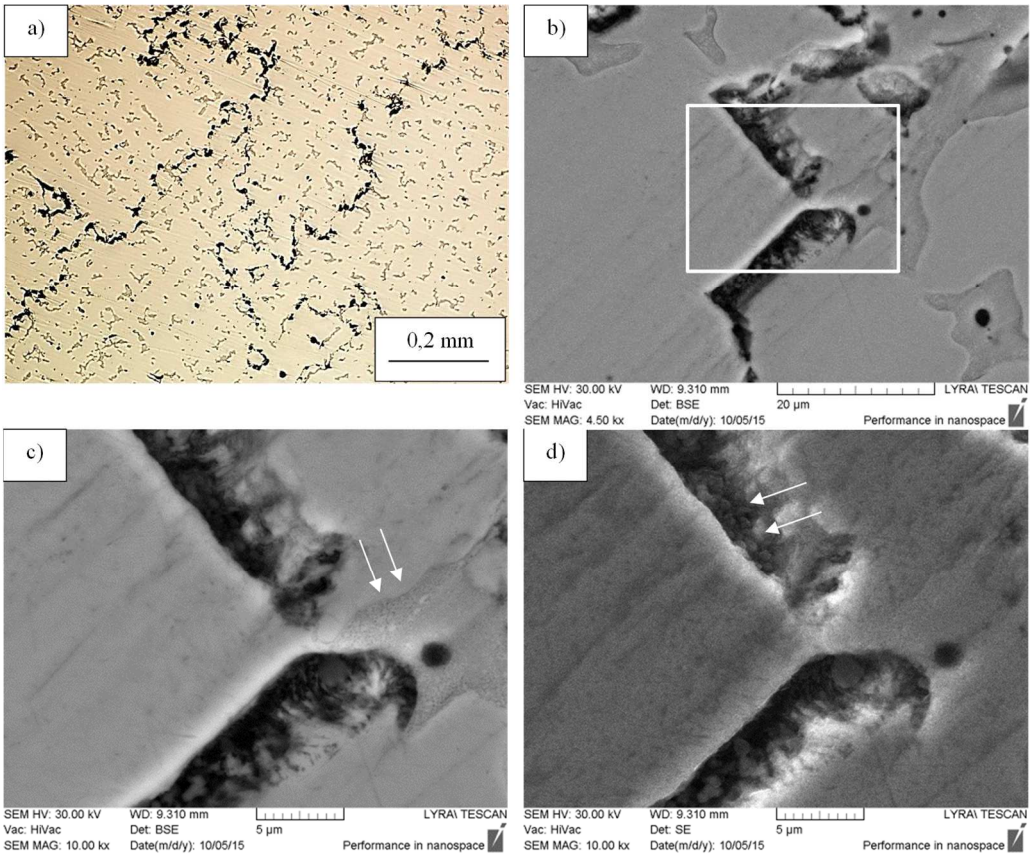


Fig. 1 Microstructure of sample (OM image), manufactured by standard casting of wax model – a). Morphology of interdendritic region of sample (SEM image), manufactured by standard casting of wax model – b) in higher magnification – c) and in back scattered electrons regime – d)

The microstructure of the sample, cast by 3D printed polymer model, is nearly the same (Fig. 2). It characterizes with dendrite morphology and too less carbides with round shape and small sizes, situated mainly inside the grains.

EDX analysis (Fig.3) shows lower content of Co (35.82% and 43.3%) and higher content of Cr (39.13% and 40.60%) and Mo (14.07% and 10,08%) as well as that of the carbon (8.51% and 5.33%) in the interdendritic areas and carbides respectively. The tendency of decreasing the Co content and increasing the Cr and Mo content in the interdendritic and carbides areas is confirmed by the following investigation of linear distribution of the chemical elements (Fig. 4). It is very clearly seen on the images of EPMA analysis shown on Fig. 5.

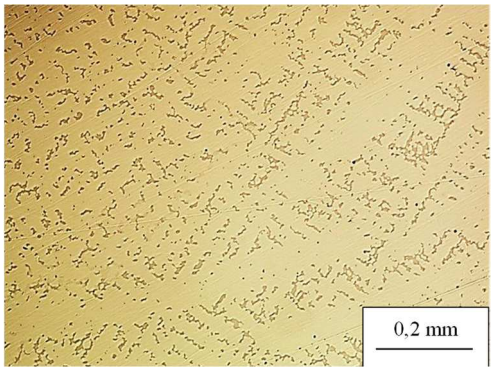
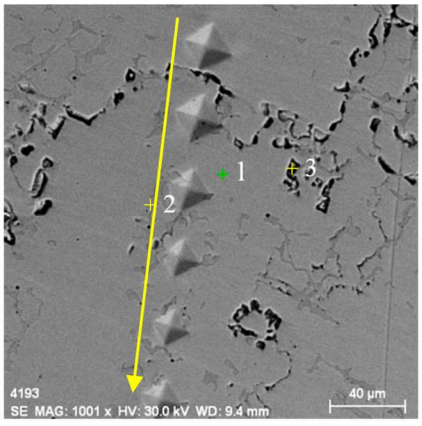
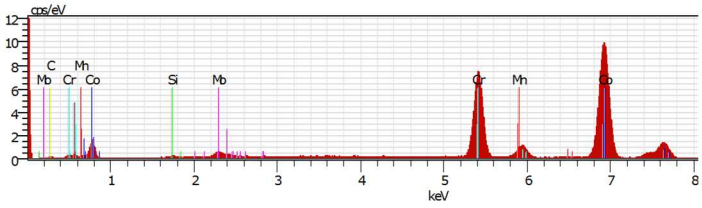


Fig. 2 Microstructure of sample, manufactured by casting of 3D printed polymer model





Element, wt. %	Co	Cr	Mo	Si	Mn	C
"Biosil"	64.8	28.5	5.3	0.5	0.5	0.4
Point 1	67.11	23.48	4.87	0.73	1.00	2.82
Point 2	35.82	39.13	14.07	1.43	1.04	8.51
Point 3	43.13	40.60	10.08	0.79	0.74	5.33

Fig. 3. Chemical composition in different points of sample, manufactured by standard casting of wax model

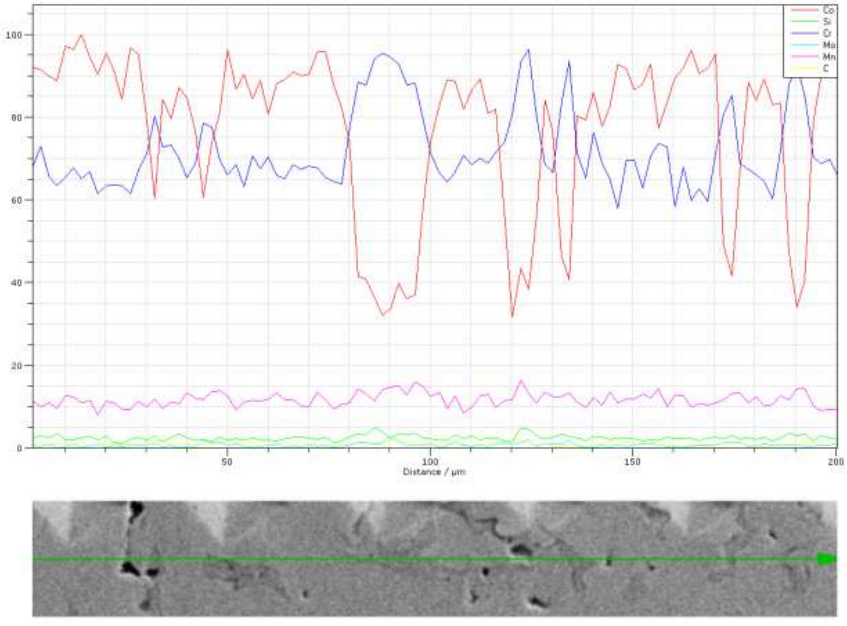


Fig. 4 Linear EDX analysis of sample, manufactured by standard casting of wax model

Concerning to the microstructure of the sample, manufactured by SLM, it possesses high corrosion resista nce and could not be etched by immersion in any reagent, given in the references. Pores with different sizes, elongated along the direction of the layers melting, are observed in the whole volume (Fig. 6a). In higher magnifications the boundaries between the molten layers (Fig. 6b) and the unmolten or partially molten powder (Fig. 6c) in the pores are clearly seen. EDX analysis shows that there is no big difference in the content of Co, Cr, Mo and carbon in different points of the sample's surface comparing to that of the unmolten powder (Fig. 7). If there is some decrease of the elements content it is due to the porous structure (Fig. 8). EPMA analysis (Fig. 9) confirms the even distribution of the chemical elements in the dense areas of the sample.

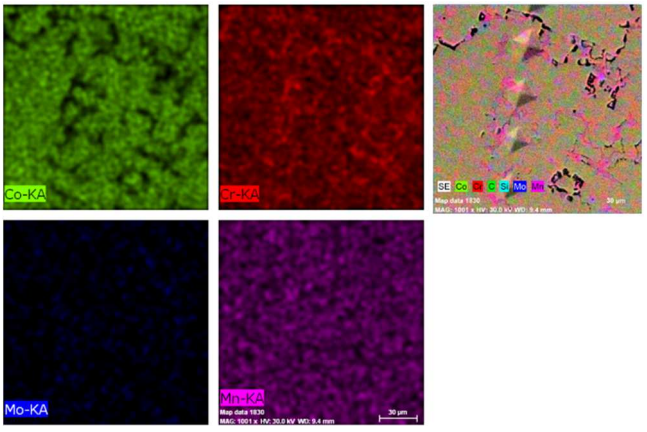


Fig. 5 EPMA analysis of sample, manufactured by standard casting of wax model.

3.2. Microhardness

Microhardness was measured along the depth of the all parts of dental bridges (Fig. 10). The average microhardness of the samples produced by different technologies is different (Fig. 11). The highest is the microhardness of all parts of the dental bridges produced by SLM – between 356 HV0,1 and 407 HV0,1, followed by the microhardness of the samples cast of 3D printed polymer models (327 HV0,1 – 343 HV0,1) and that of the samples cast by wax models, produced in silicone mold (251 HV0,1 – 274 HV0,1). The hardness distribution along depth of the samples is uneven in all parts of the cast bridges (Fig. 12a and Fig. 12b). There are high fluctuations of the microhardness values, which are in the range +/-96 HV0,1 for the samples, produced by the stadard lost-wax process, and +/-85 HV0,1 in the samples, cast by 3D printed polymer models. The hardness distribution along depth of the SLM samples is much more even (Fig.12c) with the lowest average deviation of the values +/-56 HV0,1.

4. Discussion

4.1. Microstructure

According to the Co-Cr phase diagram [3,4] the alloy with the given content should solidify in FCC γ phase which should pass through martensitic transformation to HCP ε phase in about 920°C. At about 600°C the eutectoidal decomposition of ε phase should occur according to the equation [4]:

$$\varepsilon \rightarrow Co_3Cr + Co_2Cr \quad (1)$$

But because of the very slow kinetic transformation from FCC to HCP in room temperature [5] and the alloying with FCC stabilizers like carbon, which slows the transformation rate [6], the microstructure of cast samples consists mainly of face centred cubic cobalt matrix. The γ phase is presented in the dendrites, while the interdendritic areas consist of microeutectic and primary lamellar and blocky carbides (Fig. 1a, Fig. 1b). The microeutectic represents FCC γ solid solution with intermetallic precipitations (Fig. 1c). The lower Co and the higher Cr, Mo and Si content as well as their stoichiometric ratio (Fig. 3) are evidence for presence of intermetallic phases in the microeutectic. Detailed investigation of M. Podrrez-Radziszewska et al. [4] revealed these phases are of the $Co_5(Cr,Mo)_3Si_2$ type with face centered cubic lattice. The high carbon content - 0,4% and the presence of Cr in the alloy determine carbides formation during melt solidification. They are of the $M_{23}C_6$ type which characterizes with cubic lattice [4,13,15,]. That is why it is easy for this carbide to precipitate on the dendrite boundary (Fig. 1d) and its area fraction in the cast samples to reach up to 9% [16]. As Mo solidifies in the same lattice as Cr, has similar lattice parameters and atomic radius, so it can substitute Cr in the carbides [4]. EDX analysis shows higher Cr and Mo content in the carbide formations (Fig. 3), which is evidence that the carbides are of the mixed $(Cr,Mo)_{23}C_6$ type.

The microstructure of the construction depends on the manufacturing process and technological regimes for its production. During SLM layers of metal powder are fused into a 3D detail by a computer-directed laser. The process characterizes with high heating and cooling rates, leading to fine grained microstructure of the solidified layer. As the heat is lead away through the solid body, phase transformations run in the underneath layers heated above the transition temperatures.

The volume of the molten metal depends on the volume energy density E_v, which is related to the power density N_s and the scanning speed V according to formula (2) [17]:

$$E_v = \frac{N_s}{V} \quad (2)$$

Where: *Ev* – volume energy density [J/cm^3], *Ns* – power density [W/cm^2]; *V* – scanning speed [cm/s].

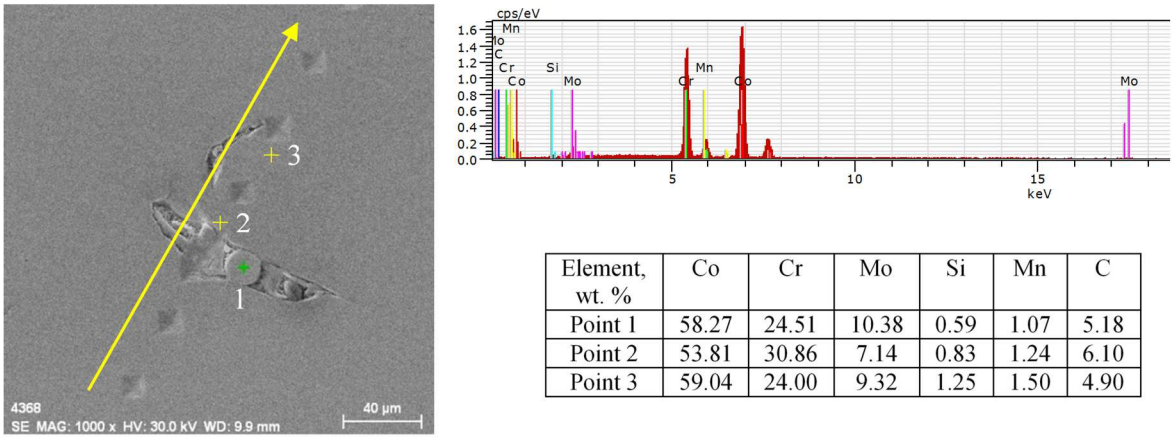
The power density N_s is calculated on formula (3) [17]:

$$N_s = \frac{4N}{\pi d^2} \quad (3)$$

Where: *N* – laser power [W], *d* – laser spot diameter [cm].

If the volume energy density E_v during the SLM process is insufficient, the incomplete melting of the deposited layer will occur. So, the lower volume energy density E_v is the main reason for the porous structure (Fig.6). This can be avoided by optimization of the technological parameters - increasing the laser power or decreasing the scanning speed.

The microstructure of SLM samples of Co-Cr-Mo alloy was investigated by Barucca et al. [13]. His team established extremely fine microstructure inside a single pool which consists of the two ε and γ cobalt phases and small carbides of the $M_{23}C_6$ (M=Cr, Co, Mo, W) types with spherical and elliptical shape and dimensions of 50-300 nm. The ε phase volume fraction is 0,49 and it forms small lamellae with 1-2 nm thickness inside the γ phase. The simultaneous coexistence of the two ε and γ phases is also reported by Yanjin Lu et al. [14]. They explain this phenomenon with the high cooling rates during SLM process and impossibility for complete γ-ε transformation.



Element, wt. %	Co	Cr	Mo	Si	Mn	C
Point 1	58.27	24.51	10.38	0.59	1.07	5.18
Point 2	53.81	30.86	7.14	0.83	1.24	6.10
Point 3	59.04	24.00	9.32	1.25	1.50	4.90

Fig. 7 Chemical composition in different points of sample, manufactured by selective laser melting

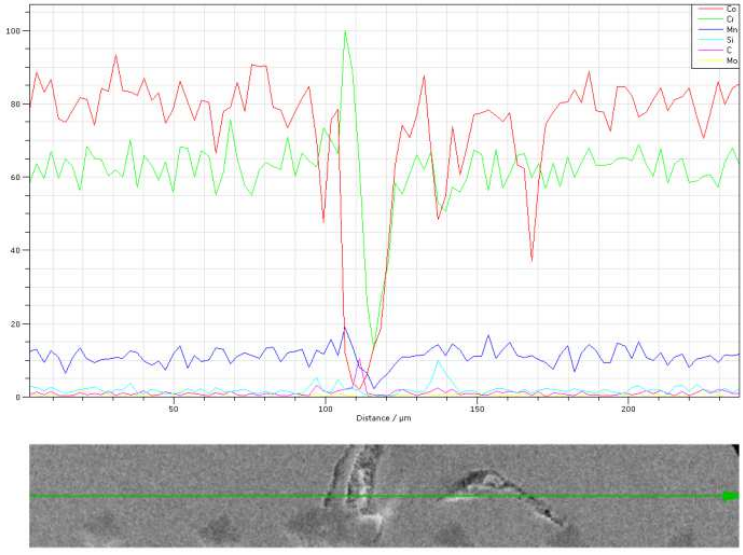


Fig. 8 Linear EDX analysis of sample, manufactured by selective laser melting.

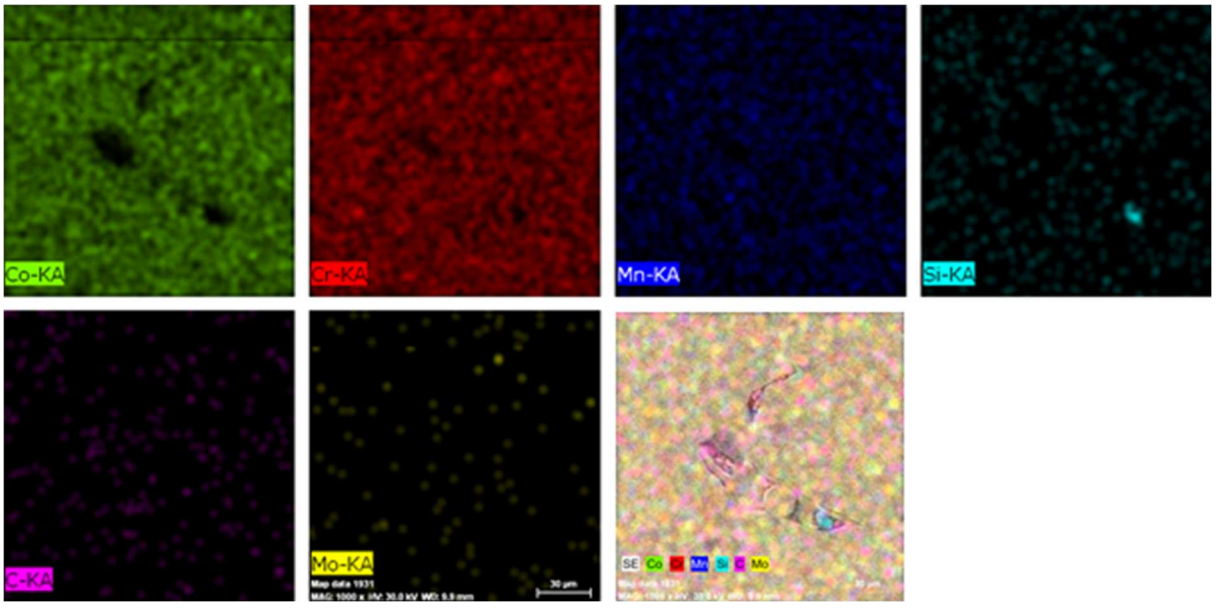


Fig. 9. EPMA analysis of sample, manufactured by selective laser melting

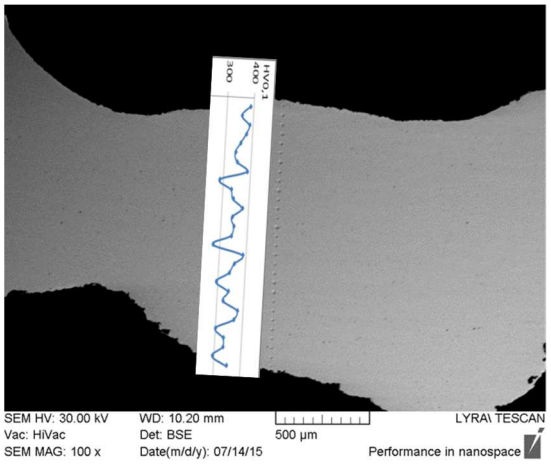


Fig. 9. EPMA analysis of sample, manufactured by selective laser melting

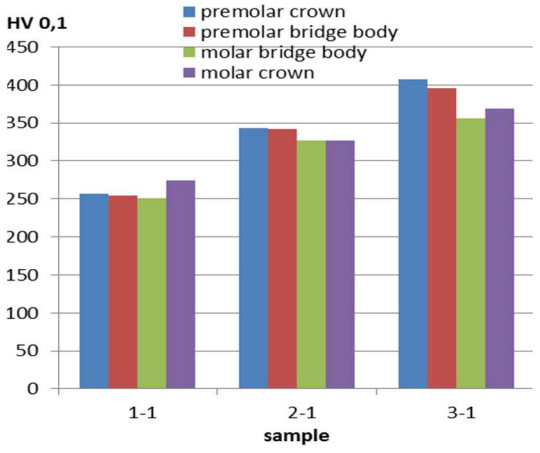


Fig. 10. Microhardness distribution along depth of occlusal surface of premolar crown of dental bridge, produced by casting of 3D printed polymer model.

But taking into account that the Co-Cr dental alloys characterize with γ phase in room temperature [4,13], complete γ-ε transformation runs during long term isothermal ageing at 750°C [18] and the influence of different factors during fast solidification of the molten pool, the most probable mechanism of ε phase formation in the surface solidified layer is athermal [13]. According to us, additional amount of ε phase could be formed in the underneath solid layers by isothermal ageing due to the continuous reheating during deposition of the molten layers on the top of the previous ones.

As the ε phase enhances the strength, corrosion and wear resistance, and the γ phase is responsible for ductility [14,18], most probably the presence of ε phase is the reason we could not do immersion etching of our SLM sample. Nearly the same composition in different points of the surface (Fig. 7) is evidence for the comparatively homogeneous microstructure resulting in solid state phase transformations due to the heating by the subsequent molten layers

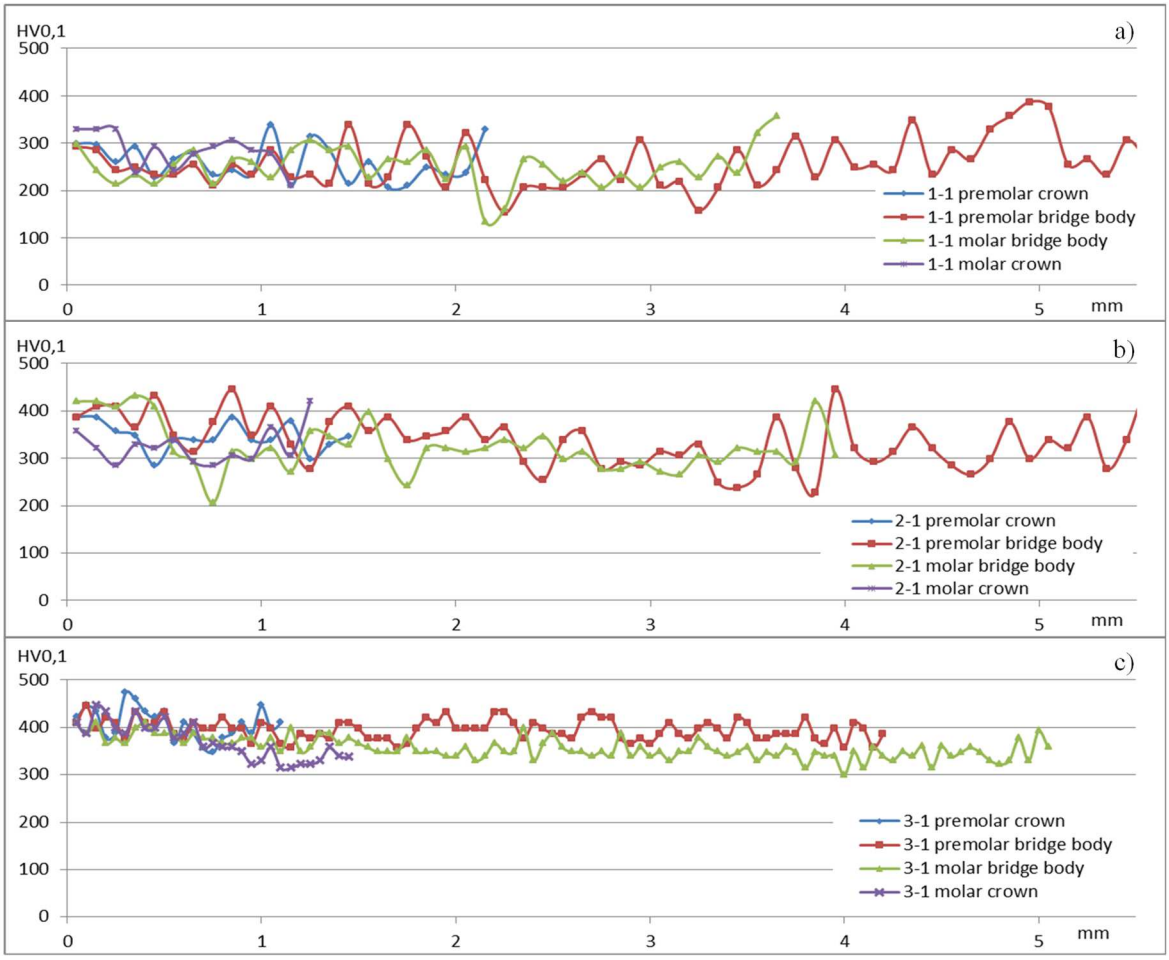


Fig. 12 Microhardness distribution along the depth of the different parts of dental bridges, manufactured by standard casting of wax model – a), casting of 3D printed polymer models – b) and selective laser melting – c).

4.2. Microhardness

The properties of the Co-Cr-Mo alloys depend on the microstructure, its morphology and composition, γ-ε ratio, presence of carbides and intermetallic precipitations [14,18]. The large grain microstructure of the sample, produced by lost-wax process of the wax model manufactured in silicon mold, determines the lowest average microhardness. In Co-Cr alloys Cr and Mo are used for solid solution strengthening [4,6,16]. One more reason for the low average microhardness is the lower Cr and Mo contents in the dendrite regions (Fig. 3), leading to insufficient matrix strengthening. The chromium additionally increase the corrosion resistance by forming a passive oxide layer on the surface and increase the hardness and wear resistance by carbide formations [6,15]. In our case there are many carbides mainly along the grains boundary and interdendritic regions (Fig. 1). They could increase the hardness of the dental construction, but we measured microhardness. As the γ phase dendrites are the largest fraction of the microstructure and it possess comparatively low strength because of the diffusion of Cr and Mo to the interdendritic regions, that is why the average microhardness of the cast samples is lower. The difference between the average microhardness of the cast samples produced of wax model and 3D printed polymer model is may be due to the different cooling conditions. The higher fluctuations of the microhardness values (Figs. 12a and 12b) are due to the inhomogeneous microstructures consisted of γ phase dendrites with lower

strength and carbides and intermetallic precipitations with high hardness in the interdendritic regions (Fig. 3).

In samples, produced by SLM and similar processes, the higher hardness is attributed to the homogeneous microstructure with fine morphology [12] and the higher volume fraction of ε phase, which can reach in some cases up to 70% [13]. The influence of carbides on the hardness change of SLM constructions is insignificant comparing to the cast samples, because in high speed processes their quantity is quite small [13]. So, due to the homogeneous microstructure there are not so high fluctuations of microhardness values in all bridge details (Fig. 12c). The difference in average microhardness of different bridge elements (Fig. 11) can be attributed to their volume. The cooling rate in smaller volumes such as premolar crown and premolar body is higher, leading to the finer microstructure and higher hardness.

4. Conclusions

In this study the microstructure and hardness of fixed dental prostheses produced of Co-Cr alloy by three different technologies – lost-wax casting of standard wax model, lost-wax casting of 3D printed polymer model and selective laser melting were investigated.

It was established that the microstructure of cast samples is dense, inhomogeneous, consisting of large grains with dendrite morphology. A large amount of lamellar and blocky carbides of different sizes are located mainly along the grain boundaries. The dendrites consist of γ phase, while the interdendritic regions - of microeutectic (Co solid solution with intermetallic precipitations) and carbides of the $(Cr,Mo)_{23}C_6$ type.

The microstructure of the SLM bridges is more homogenious concerning to the chemical composition, but porous due to the insufficient volume energy density.

The microhardness investigations showed highest average hardness of the samples, produced by SLM (356HV-407HV), followed by the hardness of the samples, cast by 3D printed models (327HV-343HV) and these, manufactured by standard lost-wax process (251HV-274HV). The measurements along depth of the samples showed nearly even microhardness distribution in the bridges, produced by SLM, and fluctuations of the microhardness values along the depth of the cast bridges due to the inhomogeneous microstructure.

As the additive technologies for production of dental restorations of wax, polymers and metal alloys are developed last years, additional investigations are needed for development of more precise technological regimes.

Acknowledgements

The 3D printed polymer models and the Co-Cr bridges, manufactured by SLM, were produced in Scientific Research Laboratory “CAD/CAM in Industry” at Technical University – Sofia with head Prof. Georgi Todorov.

Additional information

Selected issues related to this paper are planned to be presented at the 22nd Winter International Scientific Conference on Achievements in Mechanical and Materials Engineering Winter-AMME’2015 in the framework of the Bidisciplinary Occasional Scientific Session BOSS'2015 celebrating the 10th anniversary of the foundation of the Association of Computational Materials Science and Surface Engineering and the World Academy of Materials and Manufacturing Engineering and of the foundation of the Worldwide Journal of Achievements in Materials and Manufacturing Engineering.

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