Porosity and corrosion properties of CoCr alloys for dental application

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Abstract: *The paper deals with the problem of occurrence of internal defects in materials produced by SLM technology. The influence of the position of materials on the platform during the SLM on selected properties - porosity and corrosion resistance were examined. The reuse of non-compacted powder (three times recycled powder) and its effect on porosity and corrosion resistance of materials was also tested. Porosity was measured on metallographic sections in two perpendicular directions by image analysis, corrosion properties were tested by linear polarization method.*

Keywords*: CoCr ALLOY, SLM, LASER MELTING, POROSITY, CORROSION RESTISTANCE*

1. Introduction

One of the most important areas of application of SLM technology is biomedical engineering, where it is possible to use geometric freedom and tailor implants to every patient in a short time. A typical example is the production of hip joints from titanium alloys or dental implants from cobalt-chromium or titanium alloys. The technology makes it possible to produce implants with new functions - hollow structures, gradient porosity, adapted stiffness or surface structure.

One of the most significant advantages of SLM technology is the very efficient use of material, theoretically up to 100%, thanks to the possibility of recycling and reusing unmolten metal powder.

A reliable automatic supply of recycled powder during the entire SLM process is ensured by an additional modular powder supply unit (PSV) connected to the machine. This unit has a 90 liter powder tank, which is sufficient for any production process. It is fully automated, so no manual intervention is required. An integrated ultrasonic screen placed under the tank sieves the metal powder before being fed into the production process. This ensures that large particles or foreign objects do not enter the SLM process. The transport of the powder between the PSV, the SLM machine and the dismantling station is performed using vacuum technology and is fully automated. The transport, screening and storage of the powdered material take place in a closed system under an inert gas atmosphere. Contactless handling ensures maximum safety.

In addition to this system, there is also a semi-automatic screening of the metal powder in an inert gas atmosphere. The metal powder obtained from the overflow containers from the SLM process is manually transferred to the powder supply manual (PSM) station. The sieved powder is collected in separate containers under the system and is ready for further use. Oversized grain returns to the atomization process. To speed up the entire production process, the sieving process is carried out in parallel with the production itself.

Despite this well-operating system, defects, sudden changes in the surface appearance and mechanical properties of the products occur sporadically on the products. In connection with this, the question arises, whether repeated recycling of powder can lead to changes in powder properties that could affect the mechanical properties of the parts produced. It is also logical to ask another question whether the position of the product on the building platform in the SLM process will be reflected in a variation of some material properties of the product. Guzanová [1,2] and Brezinová [3] demonstrated this dependence with DMLS technology and Ti6Al4V powder. The variation of product properties depending on the platform position appears to be related to the different angle of incidence of the laser beam at the centre and at the edge of the platform, resulting in a different projection area of the beam on the powder surface and hence different energy density. Due to the fundamental similarity in operation of the laser beam in DMLS and SLM processes, it is possible to assume this dependence works also in SLM technology.

The aim of the paper is therefore to analyse the porosity, hardness and corrosion resistance of materials produced by SLM technology depending on their location on the building platform when fresh and three times recycled powder is used.

2. Materials and methods

Starbond Easy Powder 30 (Scheftner Dental Alloys, Germany), was used for test samples making. Chemical composition of powder used given in wt. % is as follow: 61% Co, 27.5% Cr, 8.5% W, 1.6% Si, and C, Fe, Mn <1%. Mechanical and physical properties of the material: $Rp_{0.2}$ 760 MPa, UTS 1090 MPa, elongation 15%, Young's modulus of elasticity 225 GPa, hardness 425 HV 10, density 8.5 g.cm^{-3}. The powder was processed at Mlab Cusing R machine, Germany. Parameters for dental applications, locked and protected by the powder manufacturer, were used in the production of the test specimens. The dimensions of test samples were 20×20×2 mm. Their placement on the build platform and designation of individual sectors, as well as the direction of movement of the recoater blade is shown in Fig. 1. Samples made from fresh, unused powder, and samples made from three-time recycled powder were evaluated. Sectors 1, 3, 5, 7 and 9 were analysed in the experimental part.

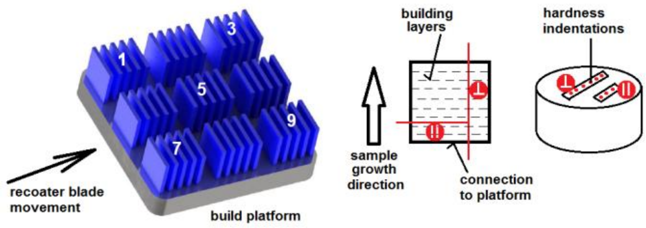


Fig. 1 *Positioning of samples, philosophy of metallographic cross-sections collection and measurement of hardness*

Metallographic sections taken in two perpendicular directions (perpendicular and parallel to the sintered layers) were used for measurement of porosity by image analysis and also for hardness test. Hardness was measured on a Shimadzu HMV-2 hardness tester under a load of 980.7 mN (HV 0.1) and full load time of 15 seconds. 30 measurements were performed in each sector and direction. Measured values were then subjected to statistical analysis by ANOVA and Tukey's test.

A Potentiostat SP 150 (Bio-Logic Sciences Instruments, France) and a 3-electrode connection were used to evaluate the corrosion properties of the material by the potentiodynamic method: working electrode (measured material), reference electrode (SCE – saturated calomel electrode), auxiliary platinum electrode. The measurement was performed in 9% NaCl solution (saline). First, the material was stabilized in solution for 30 minutes to determine the OCP (open circuit potential). Stabilisation of the corrosion system was followed by polarization ±250 mV from OCP. The corrosion current density i_{corr}, the corrosion potential E_{corr}, the corrosion rate r_{corr} and the polarization resistance Rp were determined by analysis of the measured curves.

3. Results

Porosity of materials

Metallographic sections were observed on a light microscope, analysed by image analysis, and the porosity was then expressed as a percentage of the total observed area. The results of the material porosity found in the individual sectors and directions for fresh and recycled powder are given in Table 1.

Table 1 *Porosity of materials in particular sectors and directions, %*

Sector	⊥		∥	
	fresh	recycled	fresh	recycled
1	0.35	0.99	18	19.90
3	0.37	1.25	0.94	0.41
5	3.15	5.4	4.2	7.82
7	0.33	0.25	0.2	0.24
9	0.39	0.2	0.26	0.35

The results show that increased porosity was found in sectors 1 and 5, more pronounced in the ∥ direction. In other sectors, the porosity was up to 1%. The pores in selected sectors are shown in Fig. 2.

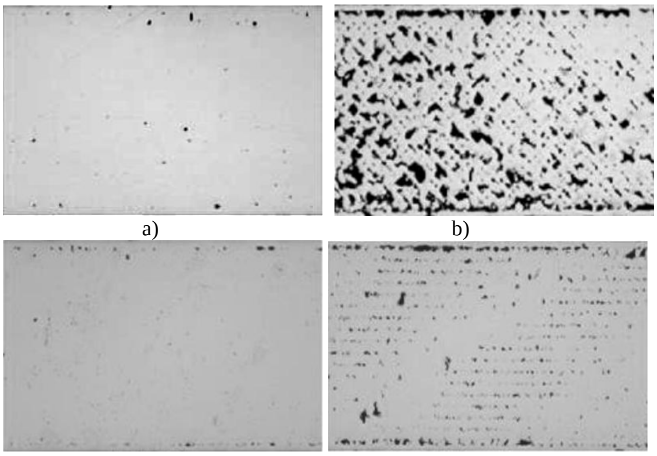


Fig. 2 *Porosity of samples made of fresh powder, a) Sector 1, direction ⊥, b) Sector 1, direction ∥, c) Sector 5, direction ⊥, d) Sector 5, direction ∥*

The increased porosity found in particular sectors of the build platform where fresh powder was processed was not coincidental, because in another, independent build platform where the recycled powder was processed, increased porosity was found in the same sectors.

Hardness of materials

Table 2 shows the hardness of materials made from fresh and recycled powder, measured in both directions, as an average of 30 measurements.

Table 2 *Hardness HV 0.1 of materials in particular sectors and directions*

Sector	⊥		∥	
	fresh	recycled	fresh	recycled
1	465	467	immeasurable	immeasurable
3	472	475	455	451
5	**428**	**435**	**439**	**433**
7	473	**482**	452	457
9	**488**	474	**458**	**463**

As can be seen from Table 2, the minimum hardness values occur in sector 5, in both directions, which corresponds with the increased porosity values. The highest hardness values appear in sectors 9 and 7, where the lowest porosity was found. In sector 1, ∥direction, hardness could not be measured because of the high porosity in the metallographic section plane.

Fig. 3 shows box-plots of hardness including mean value, standard deviation and range.

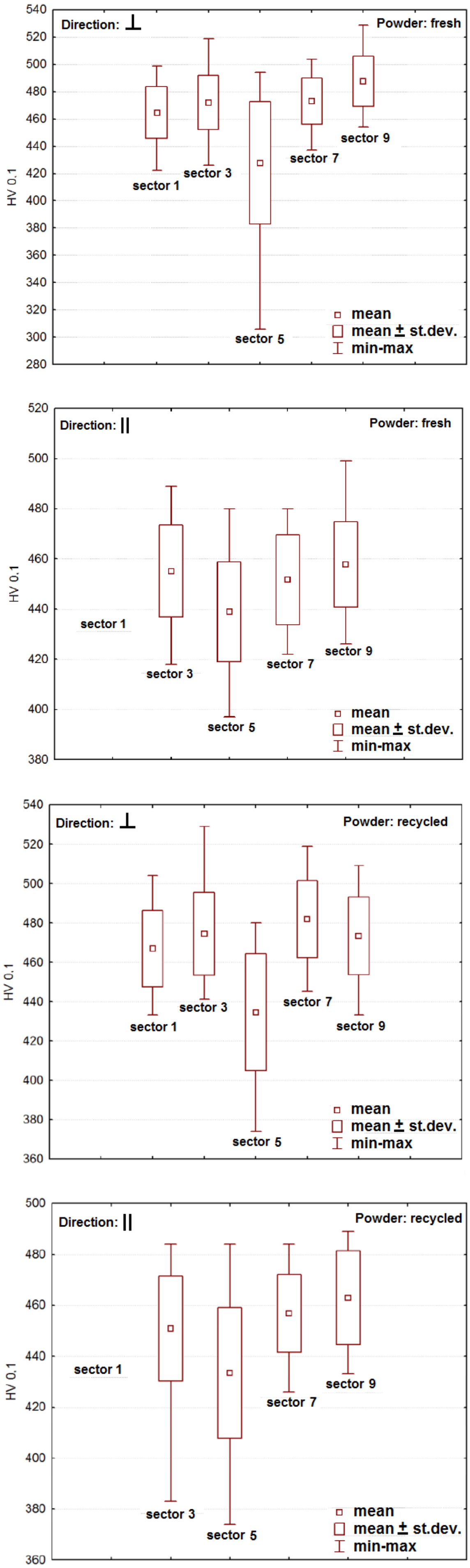


Fig. 3 *Box-plots of hardness with standard deviations and range (min-max)*

Fig. 3 shows that the hardness measured in sector 5 differs significantly from that in other sectors. This applies both when comparing directions and when comparing fresh and recycled powder. It differs not only by the mean value, which is lower than in other sectors, but also by a wider range of variation. From the observation of the individual box plots it is also clear that the variation range in the ⊥ direction is lower than in the ‖ direction. Therefore, the measured values had to be subjected to a statistical analysis to confirm or disprove the hypothesis of equality of mean values. On the one hand, comparison of hardness in two directions within each sector was performed by ANOVA (where H_0: $\mu_1 = \mu_2$; H_1: $\mu_1 \neq \mu_2$; $\alpha = 0.05$), and on the other hand Tukey's post hoc test was used for multiple mutual comparison of hardness in individual sectors within one direction (H_0: $\mu_1 = \mu_2 = ... = \mu_m$; H_1: $\mu_1 \neq \mu_2 \neq ... \neq \mu_m$; $\alpha = 0.05$). The p-value of was monitored (if p <α, hypothesis H0 is rejected). ANOVA showed p<α between two directions in every sector, i.e. hypothesis H0 is rejected and statistically significant differences in material hardness in two mutually perpendicular directions within each sector, both for fresh and for recycled powder can be pronounced. The results of the Tukey's test are shown in Table 3.

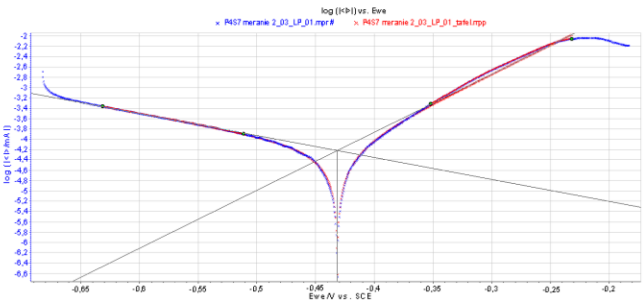
Table 3 *Results of post hoc Tukey´s test; dark cells means p<α, H0 rejected, mean values exhibits statistically significant differences*

powder		fresh					recycled				
dir	sector	S1	S3	S5	S7	S9	S1	S3	S5	S7	S9
⊥	S1	-					-				
	S3		-					-			
	S5			-					-		
	S7				-					-	
	S9					-					-
‖	S1	-	immeasurable				-	immeasurable			
	S3	immeasurable	-				immeasurable	-			
	S5			-					-		
	S7				-					-	
	S9					-					-

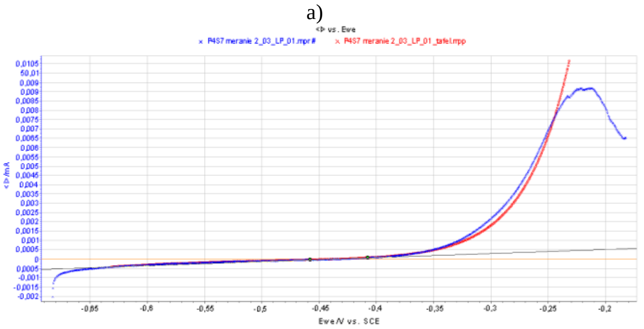
The Tukey's test confirmed in sector 5 statistically significant differences in hardness compared to all other sectors. For fresh powder in ⊥ direction, significant differences in hardness were also confirmed between sectors 1 and 9.

Corrosive properties of materials

Fig. 4 shows an example of Tafel curves and 2nd Stern analysis to determine the polarization resistance Rp.



a)



b)

Fig. 4 *a) Tafel curves,1st Stern analysis, b) 2nd Stern analysis*

Table 4 shows the calculated corrosion characteristics of the measured materials.

Table 4 *Corrosion characteristics of materials*

sector		E_{corr} [mV]	I_{corr} [μA]	bc [mV]	ba [mV]	r_{corr} [mmpy]	Rp [Ohm]
fresh powder	1	-393	0.27	264	76	0.009	83 500
	3	-367	3.84	243	106	0.131	8 260
	5	-416	1.02	208	151	0.035	42 100
	7	-373	0.46	387	61	0.016	81 700
	9	-404	0.32	253	76	0.011	154
recycled powder	1	-410	0.20	238	71	0.007	125
	3	-378	1.92	257	138	0.066	24 000
	5	-403	1.18	242	129	0.040	29 000
	7	-423	0.12	198	75	0.004	250
	9	-409	0.18	270	65	0.006	208

It is apparent from Table 4 that the corrosion rates that characterize the corrosion resistance of the material in a saline solution are at a very low level, although prior to each measurement the material was ground, cleaned and immediately transferred to the measuring cell. The oxidation of the CoCr alloy occurs almost immediately, i.e. during the measurement the electrolyte is actually in contact with the oxide layer of the material, which is manifested by a very low corrosion rate and a high polarization resistance.

4. Discussion

Hardness of materials

Hardness measurements confirmed the logical correlation with the porosity of the materials. Discovery of statistically significant differences in the hardness of materials in two mutually perpendicular directions even in sectors where the porosity was minimal has more importance. The result corresponds to similar measurements in works [1-3]. These differences can be partially eliminated, mitigated by subsequent heat treatment - annealing of materials.

Porosity

If porosity was not the goal, it is a clear defect that reduces the mechanical load-bearing capacity of the products, especially under cyclic loading. Dikova [4] notes that in the bending test of bridges made by SLM technology, the fracture spread from space between separate melted tracks, creating and developing a network of cracks across the volume starting from typical SLM defects. An important finding is that the level of porosity in different positions on the building platform varies dramatically, even if the materials on it were made under the same conditions. Implants placed in these positions will contain an unacceptable number of defects in the structure and will soon experience fatigue failure, shape collapse, etc.

Mertens [5] found that a preheated build platform can serve as an extra energy source and can help densify the processed powder when the laser beam energy seems insufficient to achieve dense components. However, the energy from the preheating does not have such a significant effect as the parameters of the laser beam (power, scanning speed).

The scanning strategy also plays a role. From Fig. 2 can be seen the skin and the core of the product. Qijan [6] notes differences in mechanical properties between core and skin, which, however, still exceed the properties of the same material processed by casting [7].

Corrosion resistance of material

The corrosion rate of the materials does not vary significantly either depending on the position on the plate or depending on the repeated use of the powder. Excellent corrosion resistance is a natural property of cobalt-based alloys. Cobalt alloys show an extremely high of corrosion resistance even in chloride surroundings due to the spontaneous creation of a chromium oxide (Cr_2O_3) passive layer within the human body [8].

5. Conclusion

The paper presents the results of research carried out on CoCr powder processed by SLM technology for dental applications. The influence of the position of the material on the build platform and the use of fresh and recycled powder on the occurrence of defects in the internal structure of the product was monitored. Sectors 1 and 5 have been shown to be critical positions on the plate where there is a rapidly increased porosity that affects the resulting hardness and consequently the fatigue life of the products. This was confirmed for two independently manufactured platforms (one made of fresh and the second from recycled powder). Significant differences in the hardness of materials in two mutually perpendicular directions can be eliminated by annealing. The question of increased porosity in these sectors should be consulted with the SLM machine manufacturer. Corrosion resistance of materials made from fresh or recycled powder is excellent. Repeated use of powder from previous SLM processes after proper sieving and treatment does not cause degradation of the properties of the products made from them.

6. References

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