Test strategy for material qualification of AM produced ceramics for implants and dental applications

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Contents

1 Summary

1.1 Role of ISFK of Montanuniversität Leoben in IAMRRI

The Chair of Structural and Functional Ceramics (ISFK) at the Department of Materials Science at the Montanuniversitaet Leoben joined the work package "Use case" at the product development phase to conduct material testing on the AM ceramics used to build a demonstrator implant.

ISFK is experienced in understanding interrelations between material microstructure and manufacturing processes and properties. Extended knowledge about these aspects has been gained on modern AM processes and materials. The competence is used to identify necessary modifications of materials and/or design considerations for specific applications. To this end ISFK is equipped for mechanical characterization of ceramics. Predefinded standardized methods are performed and critically interpreted and research is also conducted to enhance and/or develop methods directly applicable to components. ISFK is a research lab which follows standard procedures for materials testing if required, but is not an accredited testing facility.

The activities of ISFK in IAMRRI were targeted at two goals:

1) to demonstrate the suitability of ceramics manufactured by the LCM technique for implants and dental applications by considering the currently relevant standards in this area.
2) to evaluate whether AM ceramics can be characterized by the relevant material qualification standards and which aspects of the standards may interfere with special features of such ceramics, as for example limitations in specimen geometry and/or printing direction.

In this regard, the tests represent extracts of the following applicable standards:

- EN ISO 11356:2015 Surgical implants - Yttria-stabilized tetragonal zirconia (Y-TZP) ceramic materials [1].

- EN ISO 6872:2015 Dentistry - Ceramic materials [2].

1.2 Remarks on Standardisation

Interpretation of results show the challenge of coping of standard norms in novel materials development and AM productions technologies, like lithographic production technologies (LCM). Developing materials needs on the one hand more intensive research work, than that which could have been performed in the case of the use cases in WP4 and one the other hand standardisation has to open up new solutions otherwise they slow down or even prevent an innovative technology progress. Open access publications are one key for standardisation organisation to start new actions in standardisation process.

2 Activities

For the target activities, a zirconia material suitable for producing components with the LCM method (LithaCon LC210) was chosen. All Specimens were manufactured at Lithoz GmbH. Selected tests were repeated using variants of this material. The material batches used were documented and are assignable to the test specimens used subsequently. The material was sintered according to the specified sintering program. The corresponding program parameters and the maximum sintering temperature reached were documented and assigned to the test specimens. If mechanical finishing such as grinding and polishing was required prior to testing, the corresponding test specimens were manufactured with approx. 1 mm grinding tolerance.

3 Experimental

3.1 Tests according to ISO 13356

The standard ISO 13356:2015 "… specifies the characteristics of, and corresponding test methods for, a biocompatible and biostable ceramic bone-substitute material based on yttria-stabilized tetragonal zirconia (yttria tetragonal zirconia polycrystal, Y-TZP) for use as material for surgical implants." [1] Category 1 tests are required for periodic monitoring of the production; category 2 tests are necessary to prove the minimum requirements.

For the actual procedures of specific tests, ISO 13365 refers to standards for ceramic material in general and gives additional instructions for specimen preparation, numbers of specimens and specimen size. While these additional instructions are detailed for some tests, there is some flexibility for others.

The prescribed tests of ISO 13356, together with considerations arising from the necessity to investigate an AM-ceramic regarding specimens size, number, quality, … are summarized in Table 1. Some experiments were omitted because either they were performed at different facilities, necessary equipment was not available or because they were considered too laborious for the present study.

3.2 Tests according to ISO 6872

ISO 6872:2015 "… specifies the requirements and the corresponding test methods for dental ceramic materials for fixed all-ceramic and metal-ceramic restorations and prostheses." [2] Contrary to the standards for implants, this standards details all aspects of the testing methods and does not refer to other standards for general ceramic materials.

The prescribed tests of ISO 6872, together with considerations arising from the necessity to investigate an AM-ceramic regarding specimens size, number, quality, … are summarized in Table 2.

All experiments of sections 3.1 and 3.2 are described in more detail in [3], which provides also a discussion of the results.

3.3 Size effect of strength

The strength of ceramic materials depends on the volume of material that is actually loaded during the test, so-called the "effective volume"[4]. Expressions for the effective volume for common test geometries can be found in textbooks [5]. The smaller the effective volume of a specimen, the higher the measured strength will be. The effect is more pronounced for materials with a high scatter of strength (low Weibull modulus m). This is illustrated in Figure 1. For a given material, the ratio of strength as tested with the smallest allowed specimen (cross section 3.8 × 2.1 mm² in 3-point bending on a 20 mm support), σ_{smallest}, and the largest allowed specimen (cross section 4.2 × 3.2 mm² in 4-point bending on a 40 mm support), σ_{largest}, is plotted depending on the Weibull modulus m. For a typical ceramic material with $m = 10$, the small specimens will result in a ~45% higher strength than the largest specimens.

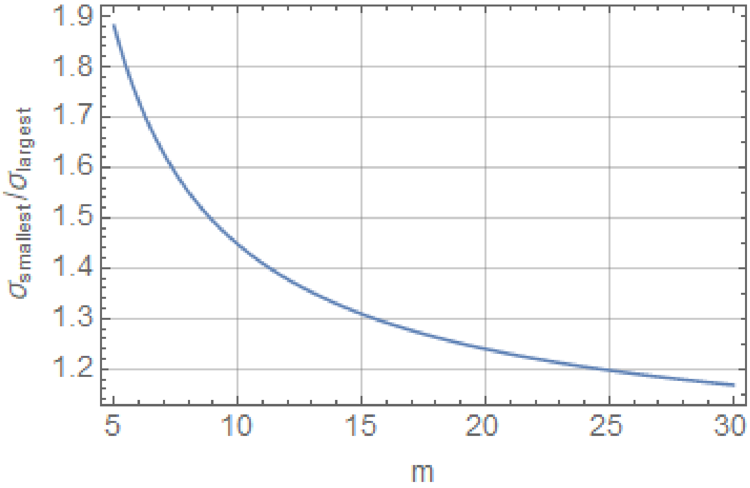

Figure 1: Relation of strength determined with two extreme specimen dimensions in dependence of the Weibull modulus *m*.

In ISO 6872, Table 1, the classification of materials for dental applications into class I to class V for applications with increasing complexity is only depending on the strength – fixed goals for each class are given in the referred table. There is however no indication, with which specimens and testing geometry this strength has to be measured. The required values can be reached much easier if small specimens are tested. This aspect is also discussed in [6]. Such an undefined situation is unsatisfactory, especially if stated in a standard.

Table 1: Tests according to ISO 13365. Standards which were followed for the present investigation are indicated in bold letter.

<table>
<tr><th>Category</th><th>Property
(reference standards or methods)</th><th>Specimen specification number for one set</th><th>Facts to be considered for AM materials</th><th>Suggested solution (for this investigation)</th></tr>
<tr><td rowspan="2">1</td><td rowspan="2">Bulk density
(ISO 18754, EN 8623-2)</td><td rowspan="2">min. 1cm^3
min. 1g</td><td colspan="2">performed at different facility</td></tr>
<tr><td>For immersion method: surface quality (avoid air bubbles sticking to surface):</td><td>ground surfaces</td></tr>
<tr><td>1</td><td>Chemical composition analysis
(ICP-OES, XRF or AAS)</td><td>piece of bar OR
piece of disc</td><td></td><td>Performed on remainders of strength tests</td></tr>
<tr><td>1</td><td>Microstructure analysis:
average grain size (SEM)
(ISO 133383-1, ASTM E112 [7])</td><td>3 – 5 discs/plates OR
3 – 5 bars</td><td></td><td>Bars (remainders of strength tests)</td></tr>
<tr><td rowspan="4">1</td><td rowspan="4">Biaxial flexural strength
(ASTM C1499)</td><td rowspan="4">10 discs
∅ 36mm
thickness 2mm</td><td colspan="2">omitted</td></tr>
<tr><td>Printing direction relative to testing direction</td><td>Standing, if there is any relation between testing and printing direction, this is the weakest direction [8].</td></tr>
<tr><td>Machined or as-printed (= as-fired) tensile surface</td><td>As-printed (=as-fired), this is the weaker state and relevant for the struts of the scaffold structure [8].</td></tr>
<tr><td>Specimen size: huge, difficult to print with LCM.</td><td>ASTM C1499 [9] allows for smaller specimens: ∅ 13mm or plates 13×13mm^2, thickness 0.7mm, max. 0.8mm, plates are easier to print than discs</td></tr>
</table>

Table 1 continued

1	Four-point bending strength (ISO 14704, ASTM C1161, **EN 843-1 [10]**)	10 bars 3×4×45 mm^3	Printing direction relative to testing direction	z (standing), if there is any relation between testing and printing direction, this is the weakest direction
			Tensile surface: Machined or as-printed (= as-fired) tensile surface?	As-printed (= as-fired), this is the weaker state and relevant for the struts of the scaffold structure. The influence of surface finish on strength and Weibull modulus may be significant. We should aim to test a condition that is relevant for state of the final part: struts in a scaffold structure will not be machined, flat top and bottom face of the part will probably be machined?
			Edges of tensile side: printed chamfers or rounded edges or machined chamfers. If printed in z direction, chamfers will have notches because of the layers	Printed round edges on all four edges
1	Weibull modulus (ISO 20501, **EN 843-5 [11]**, ASTM C1239)	30 strength specimens		Performed for four-point bending strength
1	Accelerated aging amount of monoclinic phase (XRD)	10 specimens as for strength	equipment not at hand	
2	Hardness (**ISO 14705**, EN 843-4 ASTM C1327)	see microstructure analysis		Additional loads 3kg, 10kg, 20kg

Table 1 continued

2	Young's modulus (ISO 17561, **EN 843-2 [12]**, ASTM C1331, ASTM C1198)	3 bars 3×4×45 mm^3 machined	Printing direction: should be determined parallel and perpendicular to printing direction, i.e. 2 specimen sets.	Both directions, not much information is available on the relation between Young's modulus stressing direction and printing direction, possible anisotropy is relevant for struts
2	Cyclic fatigue (ISO 22214)	min. 15 bars 3×4×45 mm^3	equipment not at hand	
2	Accelerated aging - strength	10 specimens as strength	equipment not at hand	
2	Microstructure analysis: amount of monoclinic phase (XRD)	3 – 5 discs/plates OR 3 – 5 bars		Performed on remainders of strength tests (bars)
2	Radioactivity (gamma spectrometry)		equipment not at hand	

Table 2: Tests according to ISO 6872.

Property	**Specimen specification number for one set**	**facts to be considered for AM materials and generally**	**Suggested solution (for this investigation)**
Radioactivity (gamma spectrometry)		equipment not at hand	

Table 2 continued

Flexural strength bending Weibull statistics	(10) 30 bars 2.1 ± 1.1 × 4 × variable mm^3, depends on test set-up 3-point-bending: 12 mm $< L <$ 40mm 4-point bending: 16 $< L <$ 40 mm, $l = L/4$	Specimen size: a wide range of specimen sizes and testing geometries is allowed. The size effect on strength [4] is not considered. This is detailed in section 3.3.	Largest allowed specimens tested in 4-point bending
		Number of Specimens: 10 specimens → mean value of strength, minimum required number (15) very low for proper determination of Weibull statistics	30 specimens tested
		Printing direction, tensile surface as-printed or machined, printed or machined chamfers	see line “Four-point bending strength” in Table 1.
Flexural strength biaxial (Piston-on-Ring test) Weibull statistics	(10) 30 discs ∅ 14 ±2 mm thickness 1.2 ± 0.2 mm	omitted	
		Number of Specimens: 10 specimens → mean value of strength, minimum required number (15) very low for proper determination of Weibull statistics	Test 30 specimens
		Printing direction relative to testing direction	Standing, if there is any relation between testing and printing direction, this is the weakest direction
		Machined or as-printed (= as-fired) tensile surface	As-printed (=as-fired), this is often the weaker state

Table 2 continued

Linear thermal expansion coefficient Glass transition temperature	3 bars, cylinders $5\ \text{mm} < L < 50\ \text{mm}$, $A_q < 30\ \text{mm}^2$ often: final: $5 \times 5 \times 25\ (50)\ \text{mm}^3$, parallel endfaces (machining required)	Printing direction: should be determined parallel and perpendicular to printing direction	Test both directions
		Variation of firing: ISO 6872 requires specified firing cycle in air and/or vacuum.	Only fired as usual
		Specimen size: cross section $A_q = 5\times5\ \text{mm}^2$ difficult for LCM	$3 \times 5\ \text{mm}^2$ was used
Fracture toughness SEVNB (informative appendix in ISO 6872) alternatives: **SEPB (ISO 15732) [13]** SCF (ISO 18756) CNB (ISO 24370)	5 - 10 bars $3 \times 4 \times 45\ \text{mm}^3$ machined	SEVNB is not an allowed method for 3Y-TZP ceramics, gives overestimation [14].	Use alternative method: SEPB [13]
		Printing direction: should be determined parallel and perpendicular to printing direction	Test both directions
Chemical solubility	A piece with 30cm^2 surface	Specimen shape and size	Gyroid with internal surfaces accessible to solvent

3.4 Variations of test procedures applied in the present study

For the present investigation, the 4-point bending strength was tested for the base material (LC210) and for two variants: an additional set of 30 specimens was consolidated using HIP (LC210-HIP) and another set of 30 specimens was printed using a slurry based on a different photopolymer system (LC230).

For the fracture toughness measurements, the SEPB method [13] was used. Pre-cracking was accomplished using the procedure proposed by Sglavo et al. [15].

For the determination of the coefficient of thermal expansion the procedure described in ISO 6872 was applied (one heating ramp up to 550 °C) and additional measurements were performed using a quasi-static temperature program as shown in Figure 2.

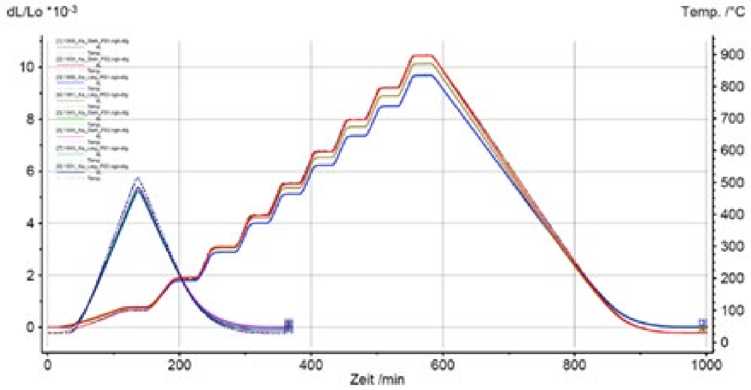

Figure 2: Temperature-time programs and relative elongation versus time for dynamic and quasi-static measurements of the linear thermal expansion coefficient.

4 Results

4.1 Properties of LithaCon LC210 and LC230

The measured properties are summarized in the following Tables 3 and 4 and in Figure 3 to Figure 7. Fracture toughness $K_{IC,SEPB}$ = 4.4. ± 0.2 $MPam^{0.5}$ irrespective of testing direction relative to printing direction. The material has a chemical solubility of 0 µm/cm³.

Table 3: Chemical composition of two specimens from two different printing jobs (67-st-f-02 and 77-l-02).

Mass-%	67-st-f-02	77-l-02
$ZrO_2 + HfO_2 + Y_2O_3$	99.0	99.0
Y_2O_3	5.1	5.1
HfO_2	1.9	1.9
Al_2O_3	0.3	0.3
Rest: other oxides	0.8	0.8

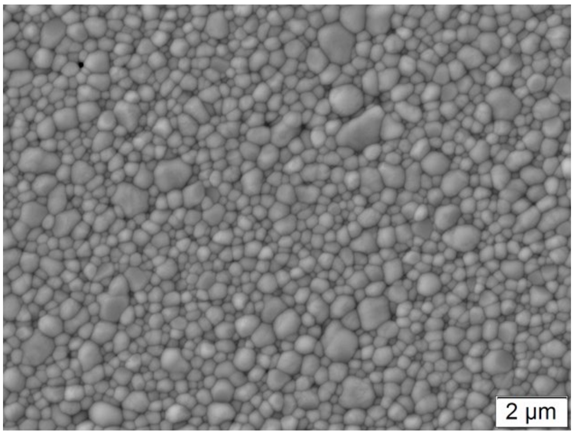

Figure 3: Microstructure, thermally etched. The grain size is 0.41 ± 0.01 µm. No monoclinic phase could be detected.

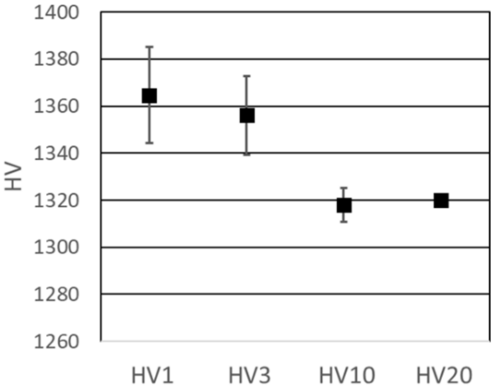

Figure 4: Vickers hardness determined with various loads.

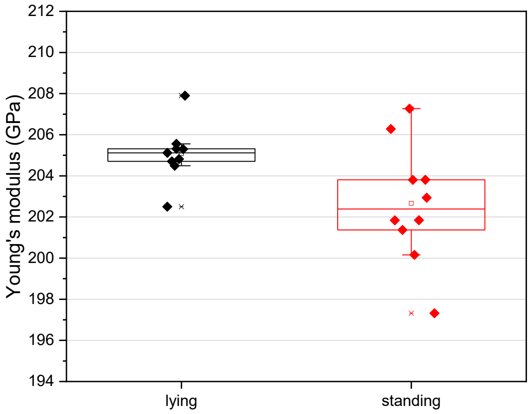

Figure 5: Young's modulus for specimens loaded in the printed layer planes (lying) and loaded normal to the layer planes (standing).

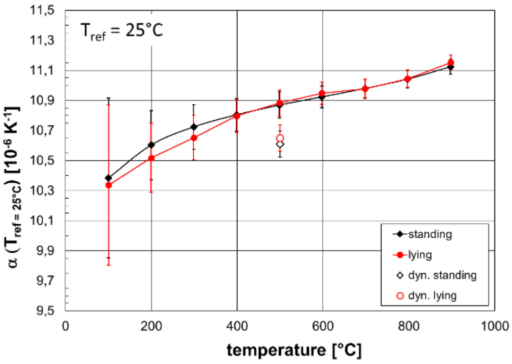

Figure 6: Technical thermal expansion coefficient for T_{ref} = 25°C for specimens printed standing and lying.

(a)

(b)

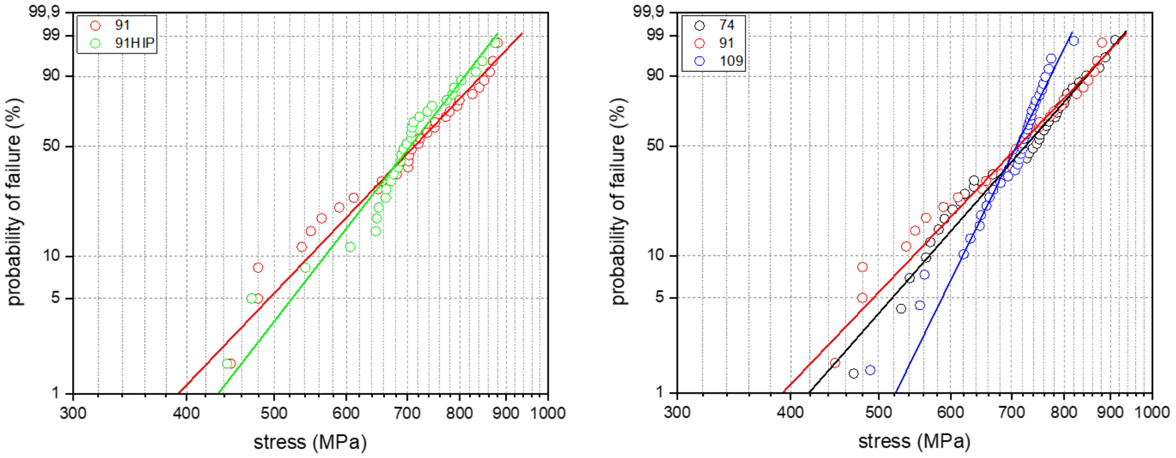

Figure 7: Weibull plots of the strength distributions (a) comparison of LC210 with LC210-HIP, (b) comparison of two sets of LC210 (74, 91) with LC230 (109).

Table 4: Parameters of the Weibull distributions for the investigated material variations.

Material	Charge	σ_0 [MPa]	90% conf.intervall for σ_0	Weibull modulus *m*	90% conf.intervall for m
LC210	Z21074	760	731 – 791	7.7	6 – 9.3
LC210	Z21091	750	715 – 786	7.0	5.3 – 8.6
LC210$_{HIP}$	Z21091	746	718 – 775	8.7	6.5 –10.6
LC230	Z21109	728	711 – 744	13.9	**4.6 – 16.7**

5 Summary

5.1 Qualification according to ISO 13356 and ISO 6872

The suitability of ceramics manufactured by the LCM technique for implants and dental applications can be analysed by comparing the measured values with the requirements given in the standards. It turns out that the strength and the scatter of strength of the investigated material do just not meet the requirements for implants. As a consequence, in regard to dental applications, the material is suitable as class IV material but not as class V material.

Table 5: Comparison of requirements according to ISO 13356 and measured quantities.

Property	Unit	Requirement	Measured
Bulk density	g cm^{-3}	≥ 6	n.a.
Chemical composition			
$ZrO_2 + HfO_2 + Y_2O_3$	mass%	≥ 99.0	99.0
Y_2O_3		> 4.5 to ≤ 6.0	5.1
HfO_2		≤ 5	1.9
Al_2O_3		≤ 0.5	0.3
other oxides		≤ 0.5	0.8
Microstructure			
grain size	µm	0.4	0.41 ± 0.01
amount of monoclinic phase	mol%	≤ 20	not detectable
Strength			
4-point bending	MPa	≥ 800	756
Weibull modulus		≥ 8	7.4
Young’s modulus	GPa	≥ 200	205.0 ± 1.4
Hardness	GPa	≥ 11.8	14.1 ± 0.2
Cyclic fatigue limit stress at 10^6 cycles	MPa	≤ 200	n.a.
Radioactivity	Bq kg^{-1}	≤ 200	n.a.
Accelerated ageing			
maximum amount of monoclinic phase	mol%	≤ 25%	n.a.
residual biaxial strength	MPa		

residual 4-point bending strength	MPa	≥ 500 MPa, $\Delta < 20\%$ ≥ 800 MPa, $\Delta < 20\%$	

Table 6: Comparison of requirements according to ISO 6872, type 2, class V materials and measured quantities.

Property	Unit	Requirement	Measured
Flexural strength	MPa	≥ 800	765
Chemical solubility	$\mu g\ cm^{-2}$	100	0
Fracture toughness	$MPam^{0.5}$	≥ 5	4.4 ± 0.1
Coefficient of thermal expansion			
$\alpha_{\text{tech, 25°C – 500°C}}$	K^{-1}		10.6 ± 0.1
glass transition temperature	°C		not detectable
Radioactivity	$Bq\ g^{-1}$	1.0 ^{238}U	n.a.

5.2 Evaluation of the feasibility of the standards for AM materials

The role of standardisation was topic in the IAMRRI project. The following chapter discusses the role of standards in ongoing research of novel AM materials. ISO 13356 and ISO 6872 were developed for monolithic ceramics with isotropic properties produced by methods other than additive manufacturing. Certain prescribed test specimens were found to be difficult to be manufactured by the LCM process and for certain test procedures not all aspects of the property spectrum of AM ceramics may be captured.

Difficulties to fulfil standard specification of are seen in the following points:

Specimen size: Biaxial flexure according to ISO 13356 is to be determined on discs with a diameter of 36 mm, which is a reasonable size if hip-implants are considered, but which is rather large if implants as considered for this use case are regarded.

Relation manufacturing-testing direction: The strength of AM ceramics may be dependent on the relation between stress direction and manufacturing direction. This suggests a treatment in the standards where specific printing direction-test direction relations for the strength specimens or a clear regulation on its documentation are missing. This may also be relevant for Young's modulus, fracture toughness and linear thermal expansion coefficient.

Scaffold structures: As shown in the use case, AM methods offer the possibility to construct implants with scaffold structures. It is still a topic of research how the mechanical properties of such structures depend on the properties of the material from which they are made. Thus a material qualification according to the above standards may have to be complemented by procedures which allow assessing the performance and reliability of such structures.

6 Literature

[1] ISO 13356, Implants for surgery - Ceramic materials based on yttria-stabilized tetragonal zirconia (Y-TZP), 2016.

[2] ISO 6872, Dentistry - Ceramic Materials, 2015.

[3] S.Z. Endt, Charakterisierung einer additiv gefertigten Zirkonoxidkeramik für Dentalanwendungen und Implantate, Masterarbeit, Department Werkstoffwissenschaft, Lehrstuhl für Struktur- und Funktionskeramik, Montanuniversität Leoben, Leoben, 2021, p. 126.

[4] D. Munz, T. Fett, Ceramics, Springer, Berlin, Heidelberg, 1999.

[5] J.B. Wachtman, W.R. Cannon, M.J. Matthewson, Mechanical Properties of Ceramics, 2nd ed., Wiley-Interscience, New York, Chichester, 2009.

[6] T. Lube, R. Danzer, Mechanical Properties and Reliability of Advanced Ceramics, in: J.Z. Shen, T. Kosmač (Eds.), Advanced Ceramics for Dentristry, Butterworth-Heinemann, Waltham, USA, 2014, pp. 173-199.

[7] ASTM E112, Standard Test Methods for Determining Average Grain Size, 1996.

[8] J. Schlacher, T. Lube, W. Harrer, G. Mitteramskogler, M. Schwentenwein, R. Danzer, R. Bermejo, Strength of Additive Manufactured Alumina, Journal of the European Ceramic Society 40(14) (2020) 4737-4745.

[9] ASTM C1499, Standard Test Method for Monotonic Equibiaxial Flexural Strength of Advanced Ceramics at Ambient Temperature, 2009.

[10] EN 843-1, Advanced Technical Ceramics - Mechanical properties of monolithic ceramics at room temperature: Part 1 - Determination of Flexural Strength, 2006.

[11] EN 843-5, Advanced Technical Ceramics - Mechanical properties of monolithic ceramics at room temperature: Part 5 - Statistical Evaluation, 2007.

[12] EN 843-2, Hochleistungskeramik - Monolithische Keramik - Mechanische Eigenschaften bei Raumtemperatur - Teil 2: Bestimmung des E-Moduls, 2006.

[13] EN ISO 15732, Fine ceramics (Advanced Ceramics, Advanced Technical Ceramics) - Determination of FractureToughness of Monolithic Ceramics at Room Temperature by the Single-edge Pre-cracked Beam (SEPB) Method, 2005.

[14] ISO 23146, Fine Ceramics (Advanced Ceramics, Advanced Technical Ceramics) – Test methods for fracture toughness of monolithic ceramics -- Single-edge V-notch beam (SEVNB) method, (similar to CEN EN 14425-5), 2008.

[15] V.M. Sglavo, P. Bosetti, E. Trentini, M. Ceschini, Sandwiched-Beam Procedure for Precracking Brittle Materials, J. Am. Ceram. Soc. 82(8) (1999) 2269-2272.