

Final Draft
of the original manuscript:

Witte, K.; Bodnar, W.; Schell, N.; Lang, H.; Burkel, E.:

**High energy X-ray diffraction study of a dental ceramics–titanium
functional gradient material prepared by field assisted sintering
technique**

In: Materials Characterization (2014) Elsevier

DOI: 10.1016/j.matchar.2014.06.018

High energy X-ray diffraction study of a dental ceramics - titanium functional gradient material prepared by field assisted sintering technique

K. Witte^{1,*}, W. Bodnar¹, N. Schell², H. Lang³, E. Burkel¹

¹Institute of Physics, University of Rostock, August-Bebel-Str. 55, 18055 Rostock, Germany

²Institute of Materials Research, Helmholtz-Center Geesthacht, Max-Planck-Str. 1, 21502
Geesthacht, Germany

³Department of Operative Dentistry and Periodontology, University of Rostock, Strempelstr.
13, 18057 Rostock, Germany

*Corresponding author. Email address: kerstin.witte@uni-rostock.de

Abstract

A functional gradient material with eleven layers composed of a dental ceramics and titanium was successfully consolidated using field assisted sintering technique in a two-step sintering process. High energy X-ray diffraction studies on the gradient were performed at High Energy Material Science beamline at Desy in Hamburg. Phase composition, crystal unit edges and lattice mismatch along the gradient were determined applying Rietveld refinement procedure. Phase analysis revealed that the main crystalline phase present in the gradient is α -Ti. Crystallinity increases stepwisely along the gradient with a decreasing increment between every next layer, following rather the weight fraction of titanium. The

crystal unit edge a of titanium remains approximately constant with a value of 2.9686(1) Å, while c is reduced with increasing amount of titanium. In the layer with pure titanium the crystal unit edge c is constant with a value of 4.7174(2) Å. The lattice mismatch leading to an internal stress was calculated over the whole gradient. It was found that the maximal internal stress in titanium embedded in the studied gradient is significantly smaller than its yield strength, which implies that the structure of titanium along the whole gradient is mechanically stable.

Keywords: Functional gradient material; Dental implants; Titanium; Field assisted sintering; High energy X-ray diffraction

1. Introduction

A dental implant is a prosthetic device applied to reconstruct the masticatory function, if the tooth root has to be extracted. Such dental implant is surgically placed in the jaw-bone from the outside and it has to replace both functions of the bone tissue, as well as the tooth itself. Therefore, the function of a dental implant is quite different at different positions i.e. inside, outside and at the boundary of the bone [1].

During the past years research and development of dental implants have been focused on implants composed of only one material, sometimes covered with a coating layer. These implants are essentially uniform in their composition and structure [2-4]. Thus, the concept of a functional gradient material (FGM) may be suitable for designing and obtaining novel

dental implants. A FGM is a composite of two or more phases, where the composition and therefore, the mechanical and physical properties, change gradually over the sample [5].

The design of such layered structures has also some disadvantages, such as complexity of scaling up the process to a mass production, difficulty in scaling up the gradient materials to large specimens or the nucleation of stress at the interfaces which reduces the reliability of the gradient under operating conditions [6]. To overcome these difficulties novel approaches have to be considered. A promising technique for the practical realisation of such gradient materials is the field assisted sintering technique (FAST), also known as spark plasma sintering (SPS) [6-8]. FAST is a rather new powder consolidation technique which applies a pulsed direct current and mechanical load to assist sintering [9-13]. The pulsed current through the die and the sample leads to a rapid heating and to short process times. But the main advantages of FAST over conventional methods like hot pressing or pressureless sintering are lower sintering temperatures, shorter exposure to elevated temperatures, no need for a binder or other additives, as well as important improvements in the properties of the sintered materials [9-10,13]. Another special feature of FAST is the ability to consolidate dissimilar materials like metallic particles, polymers or ceramics into complex nanostructured systems [6-8,10].

Nowadays, titanium and titanium alloys due to their excellent mechanical properties and high corrosion resistance are considered standard materials for dental implants with very well documented high rates of success and survival [2,14]. Potential immunologic and aesthetic drawbacks associated with titanium implants have resulted in the development of alternatives like zirconium dioxide-based dental implants. Zirconium dioxide seems to be a suitable implant material because of its tooth-like colour, mechanical properties, biocompatibility and low plaque affinity [3-4,14].

Previous experiments on binding Ti with a dental ceramics in a traditional firing process revealed that different thermal expansion coefficients of these materials and the formation of oxygen layers lead to the formation of fractures [15-16]. The application of field assisted sintering technique and the gradual change in composition of the dental ceramics - Ti gradient may overcome these problems. Moreover, the structural properties of such gradient materials combining amorphous and crystalline phases are less known and are still open to research. Therefore, it was interesting to study by high energy X-ray diffraction the structural changes i.e. the phase composition, the evolution of the crystallinity and the crystal unit edges, as well as the crystal lattice mismatch of titanium along this functional gradient material.

2. Gradient material and experimental set-up

2.1. Gradient material

As dental ceramics, the zirconium oxide-based, amorphous commercial powder Dentine VitaVM7 (Vita Zahnfabrik Bad Säckingen, Germany) with an average grain size of 18 μm was selected. The titanium powder was a pure α -phase Ti with a purity of 99.5% and an average grain size of 44 μm .

The dental ceramics-Ti functional gradient material was arranged in an eleven layer system with volume fractions of ceramics and Ti varying with 10% step in each layer, as presented in Fig. 1. All layers were designed to have a thickness of approximately 1 mm. The appropriate amounts of powders were weighted using a precise laboratory balance and, in order to ensure homogeneity, blended in grinding jars for 20 min. The obtained mixtures of powders were stacked horizontally layer by layer in a graphite die with an inner diameter of 40 mm,

according to the predefined compositional profile. The stacked material was separated from inner walls of the die and the punches with a graphite foil in order to prevent the material from reacting with the die and to ensure an electrical contact. Furthermore, to reduce radiation heat losses from the outer surface of the die, the graphite die was covered with a porous carbon felt. The application of a carbon felt also reduces possible gradients of temperature in the sample [17-18] and ensures maximal possible in-plane homogeneity of the obtained sample. The field assisted sintering technique was applied in order to consolidate the dental ceramics - Ti gradient material. The sintering procedure was performed in Tycho Sinterlab Rostock using a HP D125 unit from FCT Systeme GmbH Rauenstein, Germany.

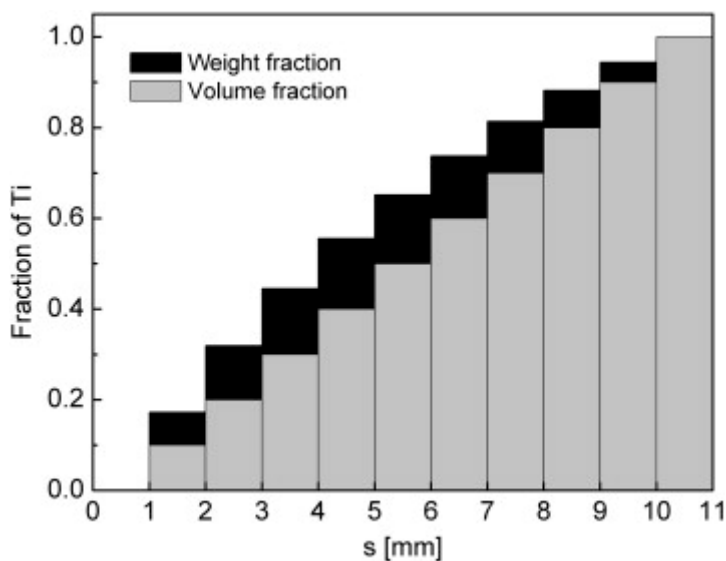


Fig. 1. Predefined compositional profile of the dental ceramics - Ti functional gradient material: the volume fraction and the corresponding weight fraction of titanium as a function of the position s in the sample.

Previous attempts of sintering the dental ceramics - Ti gradient in a one step process at 900°C with a holding time of 5 min revealed that the dental ceramics tended to darken as a result of carbon diffusion into the sample. Furthermore, a decrease of the sintering temperature to 700°C with the same process time eliminated the problem of discolouration of the dental ceramics, but in this case Ti was not completely densified. Motivated by the above, a two-step sintering procedure, i.e. pre-sintering at 500°C and main sintering at 700°C with a heating rate of 40 K/min and a holding time of 6 minutes in both cases, was introduced in order to achieve a solid, well densified material and to avoid discolouration of the dental ceramics.

The sintering process was performed in vacuum of approximately 1 mbar. During the sintering a pressure of 28 MPa was applied on the sample. In the last phase of the process, pressure was released and the sample was cooled down with a natural cooling rate of approximately 83 K/min between 700°C and 400°C. It is worth to mention that due to technical limitations, the heating process below 400°C was controlled by a thermocouple mounted in the graphite die and above 400°C by an optical pyrometer focused on a surface approximately 4 mm away from the sample, in a hole drilled in the upper graphite punch.

The post-sintered sample was cleared from the protective graphite foil using a sand blaster. For the need of further X-ray investigations a bar (cuboid) shaped specimen with dimensions of 5 mm x 1 mm x 10.5 mm (width x depth x height) was delicately and precisely cut from the middle of the sample using a diamond band saw.

2.2. Experimental set-up

High energy X-ray diffraction experiments were performed at the High Energy Material Science (HEMS) beamline P07 located at the high brilliance synchrotron radiation storage

ring PETRA III, DESY Germany. The basic design parameters of the storage ring are an energy of 6 GeV and a current of 100 mA. The source of X-rays for HEMS was a 2 m long standard PETRA undulator. The investigations were performed in the test facility EH1 using an indirectly water-cooled single bounce monochromator with a Si(220) Laue single-crystal leading to monochromatic synchrotron radiation with a wavelength $\lambda = 0.1424 \text{ \AA}$ [19-20]. The experiments were carried out in Debye-Scherrer geometry with a sample to detector distance of 1200 mm. The diffraction patterns were collected with a MAR345 image plate detector.

3. Characterisation of the gradient

3.1. Phase analysis

X-ray diffraction patterns were collected in 43 positions s every 0.25 mm over the whole gradient sample. The diffraction patterns were integrated in 5° steps and each of the obtained spectra was processed applying Rietveld refinement procedure [21] as implemented in the MAUD code [22-23].

The compositional changes in the functional gradient material are illustrated in Fig. 2 with four exemplary diffraction patterns taken at the site of pure dental ceramics ($s = 0 \text{ mm}$), 10% of Ti in dental ceramics ($s = 1.5 \text{ mm}$), 50% of Ti in dental ceramics ($s = 5.25 \text{ mm}$) and at the site of pure titanium ($s = 10.5 \text{ mm}$). In the region of pure dental ceramics the obtained X-ray patterns are typical for an amorphous material, although a number of small peaks characteristic for a crystalline structure is also observed. These peaks are originated by approximately 1.5% of crystalline zirconium oxide in the tetragonal phase.

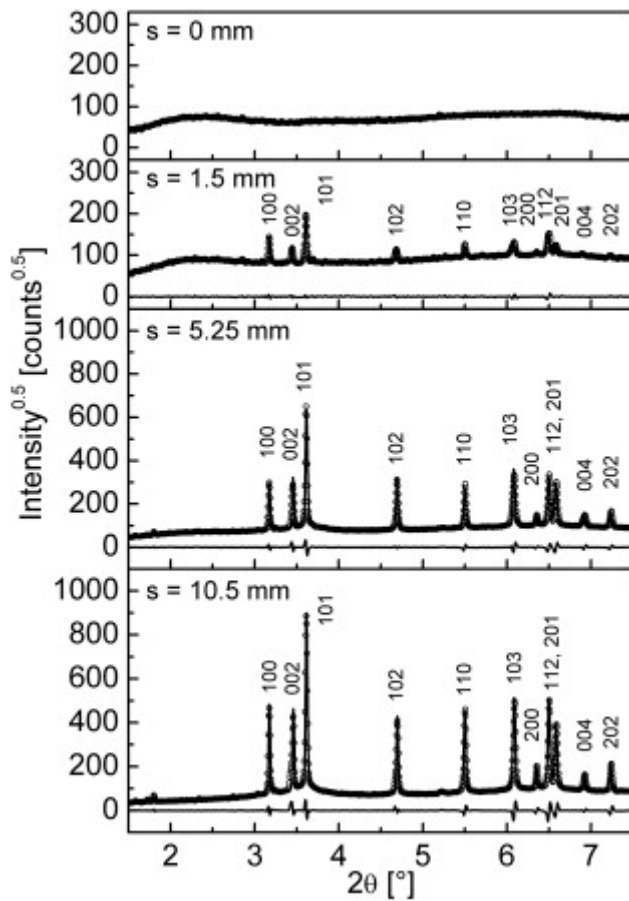


Fig. 2. Exemplary high energy X-ray diffraction patterns collected in four different positions s of the gradient: $s = 0$ mm - pure dental ceramics, $s = 1.5$ mm - 10% Ti, $s = 5.25$ mm - 50% Ti and $s = 10.5$ mm - 100% Ti. Additionally, for $s = 1.5$ mm, $s = 5.25$ mm and $s = 10.5$ mm, the fitted patterns and the differential patterns are presented. The α -Ti peaks are labeled by corresponding Miller indices.

In Fig. 2, for the position $s = 1.5$ mm, $s = 5.25$ mm and $s = 10.5$ mm additionally the fitted pattern as well as the differential pattern and Miller indices of Ti α -phase are presented. It was evidenced that titanium over the whole gradient material is mainly in α -phase. The α -phase of Ti is characteristic of a hexagonal closed packed structure belonging to the space group P63/mmc with the crystal unit edges $a = 2.95\text{\AA}$ and $c = 4.68\text{\AA}$ [24]. In Fig. 2 it is

interesting to note that in the region from 1.5° to around 3.5° ($s = 1.5, 5.25$ and 10.5 mm) small peaks can be seen. These peaks also belong to the α -phase and are originated by higher harmonics not filtered out by the optics.

Furthermore, between the (102) and the (110) peaks of the α -phase of titanium (Fig. 2, $s = 1.5, 5.25$ and 10.5 mm) an additional peak can be clearly identified. This peak belongs to the β -phase of titanium. Although it is seen best in the spectra collected in the region of pure Ti ($s = 10.5$ mm), the Rietveld refinement procedure confirmed its presence in every Ti-containing layer of the gradient. It is worth to mention that the β -phase of titanium is characteristic of a body centered cubic structure with the space group $Im-3m$ and a crystal unit edge $a = 3.28\text{\AA}$ [25]. The calculated volume ratio of α - to β -Ti is 500 and it is approximately constant in each Ti-containing layer. Thus, the β -phase of titanium in this case can be neglected.

Fig. 3 shows the structural evolution along position s in the functional gradient material. In this case each pattern was normalised to one and the square root of this normalised intensity is presented for a better visualisation of the amorphous background. On the left side the layer with pure dental ceramics and on the right side with pure titanium are placed and a gradual change from an amorphous structure to a crystalline one can be observed. Significant changes in the graph are to be noticed in the region with low concentration of Ti ($s = 1$ mm to 3 mm) where titanium is introduced to the ceramics.

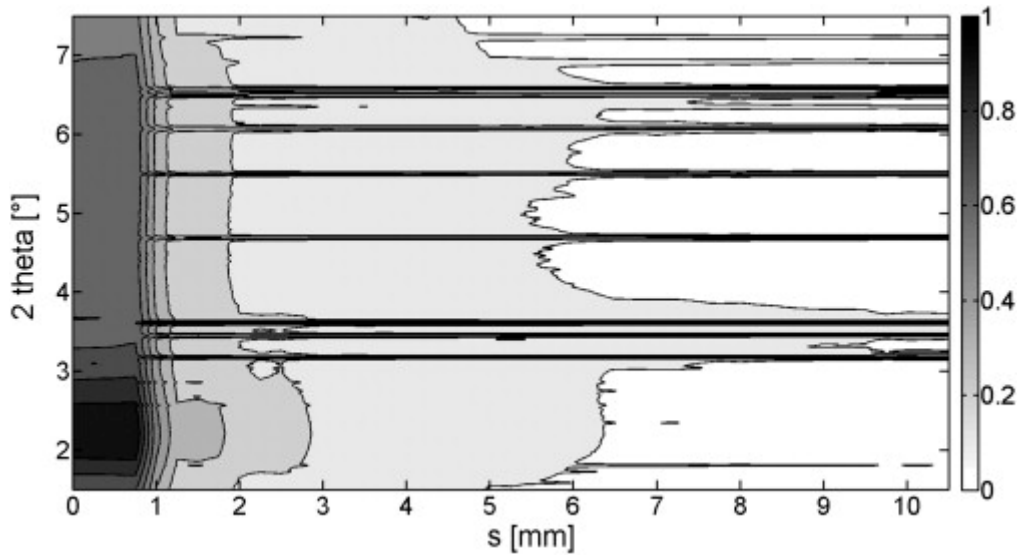


Fig. 3. Evolution of the diffraction pattern along the whole gradient sample. The right z-scale represents normalised square root of the intensity, where each pattern was normalised separately.

3.2. Crystallinity

In order to study quantitatively the evolution of the crystalline Ti in the amorphous dental ceramics it is worth to present the crystallinity γ , which can be determined using the following equation [26]:

$$\gamma = \frac{\int I_{peaks} d\theta}{\int I d\theta - \int I_{air} d\theta}. \quad (1)$$

The nominator in formula 1 presents the area under the peaks originated by all of the crystalline phases and the denominator the area under the whole spectrum, also taking into account the scattering from air. It is worth to point out that the crystallinity does not directly present the volume fraction of the crystalline phase. This is due to the fact, that every crystalline material shows also diffuse coherent as well as incoherent scattering [27].

The calculated crystallinity as a function of the position s in the gradient is presented in Fig. 4 A. The interfaces between particular layers in the gradient are marked with arrows, as they can be identified. Crystallinity shows an exponential and strongly stepwise behaviour characteristic for a layered structure. This indicates that no significant diffusion of the material occurred during the sintering procedure. Although crystallinity rises with an increasing amount of Ti, the increment decreases in every next layer. This behaviour creates a certain replica of the weight fraction of Ti in the gradient, as presented in Fig. 1.

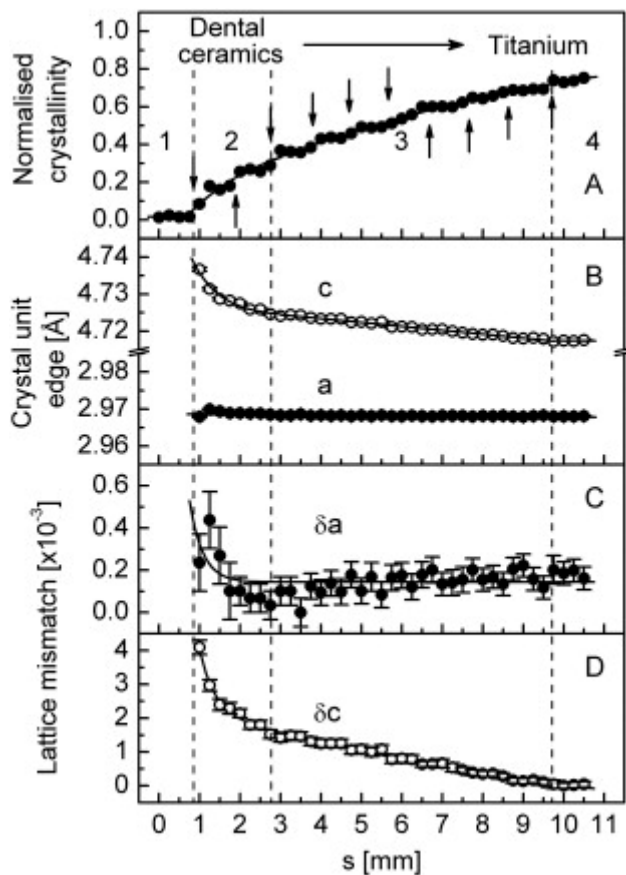


Fig. 4. Evolution of crystallinity (A), crystal unit edges a and c of α -Ti (B) and lattice mismatch δa (C) and δc (D) along the gradient. The interfaces between particular layers are marked with arrows, dashed lines represent four characteristic regions: 1 - pure dental ceramics, 2 - 10-20% Ti, 3 - 30-90% Ti and 4 - pure Ti.

Furthermore, four characteristic regions are defined due to numerical description of the calculated physical quantities, i.e. 1 - pure dental ceramics, 2 - 10-20% Ti, 3 - 30-90% Ti and 4 - pure Ti. In the first region of pure dental ceramics the crystallinity is constant with a value $\gamma = 0.02$, which is greater than zero due to a small amount of zirconium oxide in the tetragonal phase. In the second region consisting of two layers with 10-20% Ti a strong increase of the crystallinity can be observed. Here the crystallinity rises approximately by 0.29 and can be expressed by an exponential formula $\gamma = -0.64 \cdot \exp(-s/2.05 \cdot \text{mm}^{-1}) + 0.48$. Since, as a rule, the numerical parameters in the fitted formulae have no physical significance, these formulae should be treated only as a way to obtain approximate tabular data on the studied physical parameters. The third region consisting of seven layers with 30-90% Ti and the fourth region with pure Ti are treated as one, due to the fact that in the last region still a small increase of the crystallinity can be observed. This is presumably related to a diffusion of the dental ceramics into the pure titanium layer in a region of the interface. In these two regions the crystallinity rises by another 0.42 and can be described by an exponential function of the position s in the gradient $\gamma = -1.02 \cdot \exp(-s/8.85 \cdot \text{mm}^{-1}) + 1.06$.

3.3. α -Ti in the gradient

Crystal unit edges a and c of the α -titanium phase are presented in Fig. 4 B. Crystal unit edge a is approximately constant through the gradient and can be expressed with the linear function $a = 2.96861 \text{ \AA} - 0.00007 \text{ \AA/mm} \cdot s$. A small tendency to decrease can be observed only in the second region with 10-20% Ti. Nevertheless, this deviation is in the range of the obtained errors.

The crystal unit edge c exhibits significant changes in the second and third region of the gradient. In the second region with 10-20% Ti it reduces according to the exponential

formula $c = 4.7239\text{\AA} + 0.0496\text{\AA} \cdot \exp(-s/0.69 \cdot \text{mm}^{-1})$ and the total relative reduction of c in these two layers is 0.24%. Changes of c in the third region with 30-90% Ti are smaller with the total relative reduction of 0.16% per seven layers. Here, experimental points follow the linear function $c = 4.7276\text{\AA} - 0.00105\text{\AA}/\text{mm} \cdot s$. In the fourth region of pure titanium the crystal unit edge c is constant with a value $c = 4.7174(2)\text{\AA}$. It is clear from Fig. 4 B, that the crystal unit edge c is affected to a greater extent by the dental ceramics than the crystal unit edge a . These changes of c are presumably caused by a tendency of atoms diffusing from the dental ceramics, mainly consisting of Zr and O, to locate in the interstitial positions between hexagonal planes of Ti structure, ipso facto influencing c . Additionally, the presence of carbon atoms as impurities, which can diffuse from the graphite die and foils into the sample, cannot be excluded, even if no discolouration of the dental ceramics was observed. A similar effect of the diffusion of impurity atoms locating in interstitial positions between hexagonal planes in titanium alloys was previously reported elsewhere [28-29].

It is interesting to calculate the c/a -ratio, as the insertion of interstitially dissolved atoms can influence this factor which can lead to a change in the mechanical properties of the material [30-31]. For the hexagonal structure of pure titanium the c/a -ratio was found to be 1.587 [32]. In the case of dental ceramics - Ti gradient material, the c/a -ratio of α -titanium reaches a maximal value of 1.596 in the layer with 10% Ti and decreases to 1.589 in the layer with pure titanium. The c/a -ratio in the layer with pure titanium corresponds satisfactorily with the value reported in literature, but in the layer with 10% of Ti its value is significantly higher. This may suggest that an internal strain is present in the gradient.

The lattice mismatch can be interpreted as an internal strain. It is an essential parameter for the mechanical stability of the gradient. The lattice mismatch δa and δc of the crystal unit edges a and c can be determined according to the following equation:

$$\delta a(c)_i = \frac{|a(c)_i - a(c)_{Ti}|}{a(c)_{Ti}}, \quad (2)$$

where i indicates the number of spectra according to the position in a sample and Ti the derived values for the site of pure titanium. The lattice mismatches δa and δc are presented in Fig. 4 C and D, respectively. In both cases the lattice mismatch was approximated by exponential functions $\delta a = 1.438 \cdot 10^{-4} + 3.78 \cdot 10^{-3} \cdot \exp(-s/0.328 \cdot \text{mm}^{-1})$ and $\delta c = -1.73 \cdot 10^{-3} + 0.030 \cdot \exp(-s/0.357 \cdot \text{mm}^{-1}) + 0.004 \cdot \exp(-s/11.16 \cdot \text{mm}^{-1})$. Changes in the lattice mismatch are especially pronounced in the second region of the gradient material where Ti is introduced into the dental ceramics. This fact can be explained taking into account that in this layer the diffusion of atoms from the dental ceramics into the crystal structure of Ti is most probable and the probability of this diffusion decreases with an increasing volume fraction of Ti in every next layer. The maximal lattice mismatch $\delta c = 0.41\%$ was noticed in the interface between the pure dental ceramics and the second layer with 10% volume fraction of Ti. As mentioned above, the lattice mismatch can be interpreted as an internal strain. Assuming an elastic modulus of polycrystalline α -Ti of 115 GPa [32], Hook's law was applied to estimate the maximal internal stress in the studied gradient. It was found that the maximal internal stress of 472 MPa is present in the interface between the dental ceramics and the layer with 10% of Ti. Moreover, the calculated maximal internal stress is significantly smaller than the yield strength of titanium with a value between 800 MPa and 1200 MPa [32]. This implies that the structure of titanium in the second most crucial region with 10-20% Ti, and also along the whole studied gradient, is mechanically stable.

4. Summary

An eleven layer gradient material composed of a dental ceramics and Ti was successfully consolidated applying field assisted sintering technique. A two-step sintering procedure was

introduced in order to avoid discolouration of the dental ceramics. High energy X-ray diffraction studies on the gradient have been performed at HEMS beamline P07, DESY. Phase analysis revealed that the main crystalline phase present in the gradient is α -Ti. A neglectable amount of the β -Ti is also noticed in the studied sample with the α - to β -Ti phase ratio of 500.

It has been found that the crystallinity increases stepwisely along the gradient with a decreasing increment between every next layer, following the weight fraction of titanium. It shows that during the sintering procedure no significant diffusion of the materials between particular layers took place. The most intensive increment of the crystallinity is observed in the region of 10-20% titanium.

The crystal unit edge a remains approximately constant with $a = 2.9686(1) \text{ \AA}$ only with a small tendency to decrease in the region of 10-20% titanium. The crystal unit edge c exhibits more significant change with a value of $c = 4.7174(2) \text{ \AA}$ at the pure titanium side of the gradient. Changes of the crystal lattice parameters are very small (0.41% in the case of c) and could be studied only with the help of the high brilliance of synchrotron radiation.

Changes of the crystal unit edge c of Ti, and therefore the lattice mismatch δc , are presumably caused by a tendency of atoms diffusing from the dental ceramics, mainly consisting of Zr and O, to locate in the interstitial positions between hexagonal planes in the crystal structure of Ti. Moreover, the diffusion of atoms from the dental ceramics into the crystal structure of Ti is most probable in the layers with low volume fraction of Ti (10% and 20% Ti) and it decreases with an increasing volume fraction of Ti in every next layer. Hence, the changes of crystal unit edge c are mostly pronounced in the second region with 10% and 20% volume fraction of Ti.

Furthermore, the lattice mismatch over the whole gradient was analysed. It reaches maximal values for both crystal unit edges in the second layer containing 10% volume fraction of Ti. The internal stress was estimated from the lattice mismatch according to Hook's law. The maximal lattice mismatch, so the maximal internal strain present in the gradient, is in the interface between the dental ceramics and the second layer with 10% volume fraction of Ti. It was shown that the maximal internal stress present in the interface between the dental ceramics and the layer with 10% of Ti is significantly smaller than the yield strength of Ti. Hence, it implies that the structure of Ti along the whole gradient is mechanically stable.

The changes in the crystallinity and therefore composition, as well as the structural changes in the titanium phase, lead to alterations in the mechanical properties of the gradient, which require further investigation. The measurements and calculations presented, namely the evolution of the crystallinity and lattice parameters of α -Ti embedded in the gradient, may be helpful in further study, arrangement and development of such dental ceramics - titanium functional gradient material.

Acknowledgements

The assistance of Mr. Yujie Quan and Dr. Faming Zhang in the synthesis of the gradient is acknowledged.

References

[1] F. Watari, A. Yokoyama, M. Omori, T. Hirai, H. Kondo, M. Uo, T. Kawasaki, Biocompatibility of materials and development to functionally graded implant for bio-medical application, *Compos. Sci. Technol.* 64 (2004) 893.

- [2] M. Geetha, A.K. Singh, R. Asokamani, A.K. Gogia, Ti based biomaterials, the ultimate choice for orthopaedic implants - A review, *Prog. Mater. Sci.* 54 (2009) 397.
- [3] I. Denry, J.R. Kelly, State of the art of zirconia for dental applications, *Dent. Mater.* 24 (2008) 299.
- [4] J. Chevalier, What future for zirconia as a biomaterial?, *Biomater.* 27 (2006) 535.
- [5] A. Kawasaki, R. Watanabe, Concept and P/M fabrication of functionally gradient materials, *Ceram. Int.* 23 (1997) 73.
- [6] M. Belmonte, J. Gonzalez-Julian, P. Miranzo, M.I. Osendi, Continuous in situ functionally graded silicon nitride materials, *Acta Mater.* 57 (2009) 2607.
- [7] Y. Liu, Z. Jin, Electric current assisted sintering of continuous functionally graded Ti_2AlN/TiN material, *Ceram. Int.* 38 (2012) 217.
- [8] Z. Zhang, X. Shen, C. Zhang, S. Wei, S. Lee, F. Wang, A new rapid route to in-situ synthesize TiB-Ti system functionally graded materials using spark plasma sintering method, *Mater. Sci. Eng. A* 565 (2013) 326.
- [9] J.E. Garay, Current-activated, pressure-assisted densification of materials, *Annu. Rev. Mater. Res.* 40 (2010) 445.
- [10] R. Orru, R. Licheri, A.M. Locci, A. Cincotti, G. Cao, Consolidation/synthesis of materials by electric current activated/assisted sintering, *Mater. Sci. Eng. R* 63 (2009) 127.
- [11] S. Munoz, U. Anselmi-Tamburini, Temperature and stress fields evolution during spark plasma sintering processes, *J. Mater. Sci.* 45 (2010) 6528.

- [12] Z.A. Munir, U. Anselmi-Tamburini, M. Ohyanagi, The effect of electric field and pressure on the synthesis and consolidation of materials: A review of the spark plasma sintering method, *J. Mater. Sci.* 41 (2006) 763.
- [13] Z.A. Munir, D.V. Quach, M. Ohyanagi, Electric current activation of sintering: A review of the pulsed electric current sintering process, *J. Am. Ceram. Soc.* 94 (2011) 1.
- [14] J.Z. Shen, T. Kosmac (Eds.), *Advanced ceramics for dentistry*, Butterworth-Heinemann, Oxford, 2014.
- [15] J.A. Hautaniemi, H. Hero, J.T. Juhanaja, On the bonding of porcelain on titanium, *J. Mater. Sci. - Mater. Med.* 3 (1992) 186.
- [16] S. Zinelis, A. Tsetsekou, T. Papadopoulos, Thermal expansion and microstructural analysis of experimental metal-ceramic titanium alloys, *J. Prosthet. Dent.* 90 (2004) 332.
- [17] U. Anselmi-Tamburini, S. Gennari, J.E. Garay, Z.A. Munir, Fundamental investigations on the spark plasma sintering / synthesis process: II. Modeling of current and temperature distributions, *Mater. Sci. Eng. A* 394 (2005) 139.
- [18] X. Wang, S.R. Casolco, G. Xu, J.E. Garay, Finite element modeling of electric current-activated sintering: The effect of coupled electrical potential, temperature and stress, *Acta Mater.* 55 (2007) 3611.
- [19] N. Schell, A. King, F. Beckmann, H.U. Ruhnau, R. Kirchhof, R. Kiehn, M. Müller, A. Schreyer, The High Energy Materials Science beamline (HEMS) at PETRA III, *AIP Conf. Proc.* 1234 (2010) 391.
- [20] N. Schell, A. King, F. Beckmann, T. Fischer, M. Müller, A. Schreyer, The High Energy Materials Science beamline (HEMS) at PETRA III, *Mater. Sci. Forum* 772 (2014) 57.

- [21] H.M. Rietveld, A profile refinement method for nuclear and magnetic structures, *J. Appl. Cryst.* 2 (1969) 65.
- [22] L. Lutterotti, M. Bortolotti, G. Ischia, I. Lonardelli, H.R. Wenk, Rietveld texture analysis from diffraction images, *Z. Kristallogr. Suppl.* 26 (2007) 125.
- [23] L. Lutterotti, S. Matthies, H.R. Wenk, A.J. Schultz, J. Richardson, Combined texture and structure analysis of deformed limestone from time-of-flight neutron diffraction spectra, *J. Appl. Phys.* 81 (1997) 594.
- [24] R. Boyer, G. Welsch, E. W. Collings (Eds.), *Materials properties handbook: titanium alloys*, ASM International, 1994.
- [25] B.W. Levinger, Lattice parameter of beta-titanium at room temperature, *Trans. Am. Inst. Min. Met. Eng.* 197 (1953) 195.
- [26] B.B. He, *Two-dimensional X-ray diffraction*, John Wiley and Sons, Inc., Hoboken, New Jersey, 2009.
- [27] H.P. Klug, L.E. Alexander, *X-ray diffraction procedures: for polycrystalline and amorphous materials*, 2nd Edition, Wiley-VCH, 1974.
- [28] W.L. Finlay, J.A. Snyder, Effects of three interstitial solutes (nitrogen, oxygen, and carbon) on the mechanical properties of high-purity, alpha titanium, *J. Metals* 188 (1950) 1368.
- [29] H.W. Worner, The structure of titanium-tin alloys in the 0-25 at.-% tin, *J. Inst. Metals*, 81 (1953) 521.

[30] S. Anderson, B. Collen, V. Kuylenstierna, A. Magneli, Phase analysis studies on the titanium-oxygen system, *Acta. Chem. Scand.* 11 (1957) 1641.

[31] A. Alankar, P. Eisenlohr, D. Raabe, A dislocation density-based crystal plasticity constitutive model for prismatic slip in α -titanium, *Acta Mater.* 59 (2011) 7003.

[32] C. Leyens, M. Peters, editors. Titanium and titanium alloys, fundamentals and applications. Wiley-VCH; 2003.