Characterizations on Mechanical Properties and In Vitro Bioactivity of Biomedical Ti–Nb–Zr–CPP Composites Fabricated by Spark Plasma Sintering

Zheng-Yuan He^{1,2} · Lei Zhang^{1,2} · Wen-Rui Shan^{1,2} ·
Yu-Qin Zhang^{1,2,3} · Ye-Hua Jiang^{1,2} · Rong Zhou^{1,2} ·
Jun Tan^{1,2,4}

Received: 2 June 2016 / Revised: 13 July 2016 / Published online: 22 September 2016
© The Chinese Society for Metals and Springer-Verlag Berlin Heidelberg 2016

Abstract To alleviate the bio-inert of Ti alloys as hard tissue implants, Ti–35Nb–7Zr–*x*CPP (calcium pyrophosphate, *x* = 5, 10, 15, 20 wt%) composites were prepared by mechanical alloying (MA) and following spark plasma sintering (SPS). Mechanical behaviours and in vitro bioactivity of these composites were investigated systematically. Results showed that the composites consisted of β -Ti matrix, α -Ti, and metal–ceramic phases such as CaO, CaTiO₃, CaZrO₃, and Ti₃P₄. With increasing CPP content, the composites had higher strength (over 1500 MPa) and higher elastic modulus, but suffered almost zero plastic deformation together with lower relative density. When the CPP contents were 5 and 10 wt%, the compressive elastic moduli were 44 and 48 GPa, respectively, which were close to those of natural bones. However, the compressive elastic modulus of the composites increased significantly when CPP contents exceed 10 wt%, thus deteriorating the mechanical compatibility of the composites owing to more α -Ti and metal–ceramic phases. Besides, the surface of Ti–35Nb–7Zr–10CPP composite was deposited as a homogeneous apatite layer during soaking in simulated body fluid (SBF). It indicates a good bioactivity between the implant materials and living bones.

KEY WORDS: Composites; Spark plasma sintering; Microstructure; Mechanical behaviours; Bioactivity

Available online at <http://link.springer.com/journal/40195>

✉ Yu-Qin Zhang
zyqkust@163.com

¹ School of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China

² National-local Joint Engineering Laboratory of Metal Advanced Solidification Forming and Equipment Technology, Kunming 650093, China

³ Engineering Technology Research Center of Titanium Products and Application of Yunnan Province, Kunming 650093, China

⁴ IFW Dresden, Institute for Complex Materials, P.O. Box 27 01 16, 01171 Dresden, Germany

1 Introduction

Pure Ti and Ti–Al–V alloys with extra low interstitial (ELI) have been regarded as suitable structural biomaterials and are currently widely used for replacing failed hard tissues, such as artificial hip, shoulder, knee joints, and dental implants because of their unique combination of high specific strength, high corrosion resistance, and biocompatibility [1–3]. However, Ti–6Al–4V alloy could release harmful accumulation of Al and V ions in the host [4]. In addition, the poor shear strength and high elastic modulus of Ti and Ti-based alloys might result in stress shielding and implant failure. Therefore, the development of titanium alloys composed of non-toxic

and non-allergenic elements combined with appropriate mechanical properties is critical. Ti–Nb–Zr alloys have attracted considerable attentions in recent years owing to their combination of low elastic modulus and high compressive strength [5–7]. Furthermore, tissue reaction studies have identified that Ti, Nb, and Zr elements are non-toxic and non-allergenic and will not cause any dangerous reactions in the human body [8, 9]. The elastic modulus of Ti–35Nb–7Zr alloy is about 54 GPa [10], and this value is much closer to that of human bones. So the Ti–Nb–Zr alloys have been regarded as one of the most promising biomaterials. However, almost all Ti alloys including Ti–35Nb–7Zr alloy are bio-inert and thus are difficult to bond directly to living bone unlike bioactive ceramics.

Calcium pyrophosphate (CPP) has a similar composition and microstructure to human bones. Therefore, it is bio-compatible with hard tissues and exhibits good bioactivity. Nevertheless, CPP has so poor mechanical properties that it cannot be solely used in heavily loaded or large areas. Thus, it has triggered much interest in recent years to fabricate Ti-based composites combining the advantages of CPP and β -type titanium alloys [11]. It is reported that the biocompatibility of Ti–35Nb–7Zr alloy can be improved by adding CPP by spark plasma sintering (SPS) technique. However, the influence mechanism on mechanical properties and bioactivity of such composites is not well documented.

In the present work, Ti–35Nb–7Zr– x CPP composites were fabricated by SPS. The relative density and microstructure of sintered composites with different CPP contents were investigated to analyse the influence of reaction products on their mechanical properties. The bioactivity of composites was evaluated by immersion test in simulated body fluid (SBF), which helped us to understand the effects of matrix and reaction products on apatite-forming propensity of such composites.

2 Experimental

Elemental powders of Ti (99.5%, 25 μ m), Nb (99.95%, 10.5 μ m), Zr (99.5%, 25 μ m), and pure nano CPP powders were used as raw materials. The powders were prepared according to the nominal composition of Ti–35Nb–7Zr alloy and Ti–35Nb–7Zr– x CPP composites ($x = 5, 10, 15, 20$ wt%). The milling process was conducted in a mill/mixer machine (XQM-4, China) with stainless steel containers and balls (the ratio of ball to powders is 3:1) under a vacuum atmosphere for 10 h. During the milling and mixing process, anhydrous alcohol was used to maintain the balance between cold welding and fracture of the powders and to avoid cross-contamination. The blended

powders were then dried and compacted in graphite moulds (outside diameter: 30 mm, inside diameter: 20 mm, and height: 40 mm). The schematic of the equipment used for SPS is shown in Fig. 1. The green compacts were sintered by SPS system (SPS-515S, Syntex Inc, Japan) at 1000 °C for 5 min. The heating rate was 100 °C min^{−1}. The sintered sample was cooled inside the furnace to room temperature. The temperature was measured using a pyrometer focused on the measurement hole of the graphite die (see Fig. 1). The sintering was applied in a vacuum chamber at 5–10 Pa and a uniaxial pressure of 40 MPa.

The phases of the blended powders and the sintered specimens were investigated by X-ray diffraction (XRD, Bruker D8 Advance, Germany) with Cu $K\alpha$ radiation within the range of 20°–80°. The morphology of the sintered specimens was observed by scanning electron microscopy (SEM, FEI, QUANTA 600, Netherlands). The densities of the sintered specimens were calculated by using Archimedes' method. The mechanical properties of the composites were evaluated using a universal testing machine (Shimadzu, AG-X 100 KN, Japan). According to Chinese Standard GB/T 7314-2005, the specimens were processed into Φ 4 mm $\times$ 10 mm and Φ 2 mm $\times$ 10 mm for measuring compressive strength and compressive

Fig. 1 Schematic of SPS

elastic modulus, respectively. The cross-head displacement rate in these tests was 1 mm min^{-1} .

The bioactivity of the composites was assessed by soaking in SBF. The SBF was prepared by dissolving reagent grade NaCl, NaHCO_3 , KCl, $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, CaCl_2 , and Na_2SO_4 into double-distilled water and buffering at pH 7.4 at 36.5°C with tris-hydroxymethylamino-methane and hydrochloric acid [12]. Before testing, all specimens were polished and then cleaned in deionised water and an ultrasonic bath for 5 min. The specimens were soaked in SBF solution for 7 days. The solution was refreshed every 24 h to maintain a pH value of 7.4, and the temperature was maintained at 37°C during soaking. The specimens, after SBF immersion, were dried in a vacuum desiccator to remove any entrapped water molecules. After testing, the surface morphology was observed by SEM (SPM-S3400 N: Japan).

3 Results and Discussion

3.1 Mechanical Alloying Powders

Figure 2 shows the XRD patterns of Ti–35Nb–7Zr– x CPP ($x = 0, 10$ and $20 \text{ wt}\%$) powders. The XRD patterns of the powders fabricated by mechanical alloying (MA) for 10 h indicate that there are β -Ti, α -Ti, Zr, and CPP. It means that certain reactions occurred during milling. The α -Ti phases were transformed into β -Ti phases due to the β -Ti stability-inducing elements (Nb and Zr) during the milling process, which is in agreement with that observed by Wang *et al.* [13]. However, when the CPP was added, the transformation of α -Ti to β -Ti could be depressed. So the peaks of α -Ti were boosted, while those of β -Ti were weakened

with increasing CPP content. However, the CPP powders were almost not decomposed during milling.

3.2 Relative Density

Figure 3 shows the relative density of sintered Ti–35Nb–7Zr alloy and Ti–35Nb–7Zr– x CPP composites with different CPP contents. The relative density of sintered Ti–35Nb–7Zr– x CPP composites decreases from 98.9 to 96.1% with increasing CPP content, which are lower than that of Ti–35Nb–7Zr alloy. It could be deduced that the CPP ceramic decreased the SPS sintering ability and thus increased the number of flaws in the sintered composites, which led to high porosity in the specimens. These results suggested that too much CPP impaired the densification of Ti–35Nb–7Zr– x CPP composites. The trend in densification was consistent with that investigated by Woo *et al.* [11]. However, the densification was higher because of increasing milling time (10 h) leading to finer particles, thus affecting densification and sintering ability.

3.3 Mechanical Behaviours

The mechanical behaviour of the sintered specimens was investigated by compressive testing as shown in Fig. 4. It can be seen that the Ti–35Nb–7Zr alloy has a high yield strength of about 1300 MPa combined with a large plastic deformation. When the CPP content is 5 wt%, the yield strength increases over 1700 MPa. However, the plastic strain decreases significantly. With increasing CPP content, the composites are brittle when the CPP content exceeds 5 wt%.

Fig. 2 XRD patterns of Ti–35Nb–7Zr– x CPP ($x = 0, 10, 20 \text{ wt}\%$) powders

Fig. 3 Relative density of the sintered Ti–35Nb–7Zr alloy and Ti–35Nb–7Zr– x CPP composites ($x = 5, 10, 15, 20 \text{ wt}\%$) at 1000°C

Fig. 4 Compression stress-strain curves of Ti-35Nb-7Zr alloy and Ti-35Nb-7Zr-*x*CPP composites (*x* = 5, 10, 15, 20 wt%)

The effects of CPP content on the compressive strength and compressive elastic modulus of sintered Ti-35Nb-7Zr alloy and Ti-35Nb-7Zr-*x*CPP composites are shown in Fig. 5. The compressive strength of Ti-35Nb-7Zr alloy is 1923 MPa, but the compressive strength of the Ti-35Nb-7Zr-*x*CPP composites decreases to 1700 and 1525 MPa when CPP contents are 5 and 10 wt%, respectively. However, when the CPP content is between 15 and 20 wt%, the compressive strength of the sintered composites increases to 1581 and 1680 MPa, respectively. It should be mentioned that the strength of Ti-35Nb-7Zr-*x*CPP composites is higher than that of ultrafine-grained Ti (1100 MPa) [14], thus meeting the requirements of biomedical implant design. Contrary to the tendency of the strength, the compressive elastic modulus of Ti-35Nb-7Zr-*x*CPP composites consistently increases from 42 to 66

Fig. 5 Compressive elastic modulus and compressive strength of Ti-35Nb-7Zr alloy and Ti-35Nb-7Zr-*x*CPP composites (*x* = 5, 10, 15, 20 wt%)

GPa with increasing CPP content. However, the elastic modulus of the sintered specimens significantly increases when the CPP content exceeds 10 wt%, which could result in stress shielding when used as implant materials. The elastic modulus of composites with 5 and 10 wt% CPP varies from 44 to 48 GPa, which is slightly higher than that of the original Ti-35Nb-7Zr alloy (42 GPa), and is close to that of natural bones (10–30 GPa), indicating good mechanical compatibility.

Figure 6 shows the XRD patterns of the sintered specimens. The α -Ti still remains in all sintered composites except for Ti-35Nb-7Zr alloy. However, the α -Ti peaks emerge with increasing CPP content. When the CPP contents are 15 and 20 wt%, the peaks of α -Ti phase become stronger (Fig. 6d, e). This was because more CPP powders were present around the Ti powders and β -Ti stabilization elements (*e.g.* Nb and Zr) because of the lower intensity of diffusion among the Ti, Nb, and Zr during sintering. Thus, the transformation from α to β phase could be hindered. In other words, the amount of α -Ti phase increased due to the hindering effects of CPP during the process of diffusion for β -Ti stabilization elements. Furthermore, the interstitial α -stabilizer (*e.g.* O) decomposed from CPP might hinder the transformation from α to β phase [15, 16]. As a matter of fact, α -Ti could improve the elastic modulus of titanium alloy. Therefore, the content of α -Ti phases in Ti-35Nb-7Zr-*x*CPP composites increased, leading to the increased compressive elastic modulus from 44 to 66 GPa.

However, the dominated phase of sintered Ti-35Nb-7Zr-*x*CPP composites was β -Ti, which was known to decrease Young's modulus of Ti alloys. In addition, the XRD patterns show metal-ceramic phases such as CaO,

Fig. 6 XRD patterns of **a** Ti-35Nb-7Zr alloy, **b** Ti-35Nb-7Zr-5CPP, **c** Ti-35Nb-7Zr-10CPP, **d** Ti-35Nb-7Zr-15CPP, **e** Ti-35Nb-7Zr-20CPP

CaTiO_3 , CaZrO_3 , and Ti_xP_y , which were formed during the sintering process. The sintering reaction could be expressed by Eq. (1) [11], Eq. (2), and Eq. (3) [17]:

These results suggested that the phase composition of sintered Ti–35Nb–7Zr–CPP composites was affected by CPP content. Too much CPP could not only reduce the stability of β -Ti but also increase the number of metal–ceramic phases due to the reaction between the metal elements and CPP. Thus, the densification of the composites decreased, which was harmful to their mechanical properties, and it was, therefore, necessary to control the CPP content to within an optimum range.

Figure 7 shows the SEM–BSE (backscattered electron) images of sintered Ti–35Nb–7Zr alloy and Ti–35Nb–7Zr– x CPP composites with different CPP contents. One can see that the Ti–35Nb–7Zr alloy is mainly composed of Ti- and Nb-rich regions: these regions appear to be dark grey or grey and white, respectively (Fig. 7a). When 5 wt% CPP is added, the grain sizes in Ti- and Nb-rich regions decrease, and small holes appear. Acicular phases can be observed around the grain boundaries (see red arrows in Fig. 7b, c). More CPP addition introduced more holes and smaller

grains as shown in Fig. 7d, e. When the CPP content exceeds 10 wt%, a net-like structure can be seen in the Ti matrix (Fig. 7e) and in a locally magnified view (Fig. 7f), much finer grains appear. EDS spectra of points A, B, and C in Fig. 7 are shown in Fig. 8. Point A is located in a porous area which mainly consists of Ca, P, and some metal elements. Moreover, the acicular phases, as seen in Fig. 7c, are composed of Ti, Ca, P, and O. This demonstrates that some Ca and P gather in holes, and the acicular phases with high P and Ca concentrations begin to grow in the Ti matrix when the CPP content is either 5 or 10 wt%. This phenomenon is accelerated due to the CPP content exceeding 10 wt%, which results in net-like phase growth in the Ti matrix. By EDS analysis of point C, shown in Fig. 8, the net-like phases consist of Ti, Nb, Zr, Ca, P, and O.

The number of tiny holes in the composites increased due to the difference in thermal expansion coefficient between the ceramic and the metal phases. Thus, the ratio of pores increased with increasing CPP content, causing a reduction in relative density, as described in Fig. 3. Meanwhile, the holes would be beneficial for the induction of osteocyte growth [18]. Besides, Ca and P were mainly distributed around the holes or substrate, which would further induce osteocyte growth, as is well known that Ca and P are the main elemental constituents of CPP. A certain Ca and P content would improve the bioactivity of Ti alloys. However, more than 10 wt% CPP addition would

Fig. 7 SEM–BSE images of **a** Ti–35Nb–7Zr alloy, **b** Ti–35Nb–7Zr–5CPP, **c** Ti–35Nb–7Zr–10CPP, **d** Ti–35Nb–7Zr–15CPP, **e**, **f** Ti–35Nb–7Zr–20CPP

Fig. 8 EDS spectra of points A, B, C in Fig. 7

lead to the incorporation and diffusion of the bio-ceramic elements into the Ti matrix, as shown in Fig. 7d–f. This affected the mechanical properties of the composites: the finer grains and metal–ceramic phases increased the compressive strength, but the compressive elastic modulus increased mainly due to the hard phases, such as CaO, CaZrO₃, CaTiO₃, and so on.

During the SPS process, the powders of Ti–Nb–Zr, without CPP, were charged with pulsed current, and the high temperature led to melting and evaporation among the particles as the powders had good conductivity. Under axial pressure, the powders were rapidly fused together by SPS. Because of the presence of elemental Nb and Ti, large-grained β -Ti phases formed. When the CPP was added to the Ti alloy, the sintering mechanism could be interpreted as shown in Fig. 9. With increasing CPP content, the electrical conductivity of the powders decreased, so that the evaporation and melting on the surface of the particles diminished in intensity. Pulsed current in the subsequent sintering process could not directly penetrate the specimens, which were sintered by heating of the graphite mould and heat exchange between metal elements. The new phases formed through the reaction between CPP and Ti, and impeded the formation of continuous β -Ti zones, then weakened the stability and reinforcement effect of Nb and Zr in β -Ti phases, and thus increased the amount of residual α -Ti phases.

Fig. 9 Sintering mechanism of Ti–35Nb–7Zr–xCPP powders during SPS process

3.4 In Vitro Bioactivity

Figure 10 shows the surface morphologies and phase composition of Ti–35Nb–7Zr alloy and Ti–35Nb–7Zr–10CPP composite after 7-day immersion in SBF at 37 °C. The Ti–35Nb–7Zr alloy, expect for a few bright particles observed randomly on the surface, exhibits no growth of apatite layers after immersion for 7 days as shown in Fig. 10a. A magnified view of a bright particle, grown on the grain boundary of the Ti matrix, is shown in Fig. 10b. However, Ti–35Nb–7Zr–10CPP composite is homogeneously covered by a dune-like apatite layer, indicated in Fig. 10c, d, which changes the original surface morphology of composite completely. A typical magnified view of the area surrounding the tip of the large apatite particles (Fig. 10d) shows globular particles covering the entire surface of the composite and forming a layer thereon. The EDS analysis of point A shows high intensities of Ca and P with a Ca/P atom ratio of 1.59 (Fig. 10e), which is close to the ratio of hydroxyapatite (1.67). The bone-like apatite layer has a structural form like that of hydroxyapatite, in which case this epitaxy would facilitate, without any external stimulant, osseointegration between the implant and human bone.

This phenomenon could be associated with Ca and P ionic dissolution of metal–ceramic phases in the composite [19, 20]. Both Ca and P ions dissolved on the local area of the composite surface, which induced ions such as Ca²⁺, OH[−], PO₄^{3−}, and HPO₄^{2−} to deposit by electrostatic incorporation, as indicated in Fig. 11. This phenomenon boosted local supersaturation of Ca and P ions, inducing the nucleation of bone-like apatite crystals. Besides, the tiny holes formed with the addition of CPP, which made the boundary between each tiny hole and the Ti matrix be a potential nucleation site. The boundary was an energy concentration area; it could, therefore, provide the power for the nucleation and growth of bone-like apatite, which was a key method for the formation of the apatite particles on Ti–35Nb–7Zr alloy surface during soaking. The surface of Ti–35Nb–7Zr alloy, however, had limited boundaries and could not release Ca and P ions to induce the formation of numerous bone-like apatite crystals, which is reflected in Fig. 10a, b. Furthermore, the Ti suboxides could be hydrated to form Ti–OH groups on the

Fig. 10 Surface morphologies of samples after 7-day immersion in SBF at 37 °C: **a, b** Ti-35Nb-7Zr alloy, **c, d** Ti-35Nb-7Zr-10CPP composite, **e** EDS of an apatite particle

composite surface in the SBF according to the Eq. (4) [21], The Ti-OH groups could facilitate the apatite formation in the SBF by electrostatic potential interaction [22]. Thus, the surface of composites, with CPP addition, soaking in SBF was beneficial to the nucleation of bone-like apatite. Once nucleation completed, the growth would proceed spontaneously. Numerous bone-like apatite particles developed to form a homogeneous, dense layer on the surface of the Ti-35Nb-7Zr-10CPP composite after SBF immersion.

It is reported that a bone-like apatite layer precipitates on the surface of bioactive materials in the human body, which

plays an essential role in forming the chemical bond between the bioactive material and living bone [23, 24]. Hence, the Ti-35Nb-7Zr-*x*CPP composite has a better bioactivity than that of the Ti-35Nb-7Zr alloy without CPP.

4 Conclusions

In this work, biomedical composites of Ti-Nb-Zr with different CPP contents (5, 10, 15, and 20 wt%) were fabricated by milling for 10 h and then sintered by SPS technique, which was suitable for hard tissue implant to shun stress

Fig. 11 Schematic mechanism for apatite formation on surface of the composites

shielding and bio-inert. The following conclusions can be drawn:

1. The composites consisted of β -Ti matrix, α -Ti, and reaction products (metal–ceramic phases) such as CaO, CaTiO₃, CaZrO₃, and Ti_xP_y when CPP was added.
2. More CPP addition introduced more holes and finer grains. When the CPP content exceeded 10 wt%, the metal–ceramic phases grew in the Ti matrix and formed net-like structure, deteriorating the mechanical properties of composites.
3. The compressive elastic modulus of the composites was significantly increased when the CPP was added due to the increasing content of α -Ti and metal–ceramic phases. However, when the CPP content exceeded 10 wt%, the elastic modulus of the sintered composites significantly increased, which could result in stress shielding when used as implant materials.
4. The Ti–35Nb–7Zr–10CPP composite was immersed in SBF, and a dense apatite layer was formed thereon, indicating a better bioactivity than that of Ti–35Nb–7Zr alloy without CPP.

Acknowledgments This work was supported by the National Natural Science Foundation of China (No. 31160197), the Innovation Platform Construction Project for Science and Technology, Yunnan Province (No. 2013DH012), and the Analysis and Testing Foundation of Kunming University of Science and Technology (No. 2016T20090120).

References

- [1] A. Biswas, L. Li, U.K. Chatterjee, I. Manna, S.K. Pabi, J. Dutta Majumdar, *Scr. Mater.* **59**, 239 (2008)
- [2] M. Long, H.J. Rack, *Biomaterials* **19**, 1621 (1998)
- [3] B.Q. Li, X. Lu, *Acta Metall. Sin. (Engl. Lett.)* **27**, 338 (2014)
- [4] Y. Okazaki, Y. Ito, K. Kyo, T. Tateishi, *Mater. Sci. Eng., A* **213**, 138 (1996)
- [5] Z.M. Li, B.L. Zheng, Y.T. Wang, T. Topping, Y.Z. Zhou, R.Z. Valiev, A.D. Shan, E.J. Lavernia, *J. Mater. Sci.* **49**, 6656 (2014)
- [6] A.L.R. Ribeiro, R.C. Junior, F.F. Cardoso, R.B. Fernandes Filho, L.G. Vaz, *J. Mater. Sci. Mater. Med.* **20**, 1629 (2009)
- [7] V.A.R. Henriques, E.T. Galvani, S.L.G. Petroni, M.S.M. Paula, T.G. Lemos, *J. Mater. Sci.* **45**, 5844 (2010)
- [8] A. Fukuda, M. Takemoto, T. Saito, S. Fujibayashi, M. Neo, S. Yamaguchi, T. Kizuki, T. Matsushita, M. Niinomi, T. Kokubo, T. Nakamura, *Acta Biomater.* **7**, 1379 (2011)
- [9] M.A. Baker, S.L. Assis, O.Z. Higa, I. Costa, *Acta Biomater.* **5**, 63 (2009)
- [10] J.M. Chaves, O. Florêncio, P.S. Silva Jr., P.W.B. Marques, S.G. Schneider, *J. Alloys Compd.* **616**, 420 (2014)
- [11] K.D. Woo, S.H. Park, J.Y. Kim, S.M. Kim, M.H. Lee, *Korean J. Mater. Res.* **22**, 150 (2012)
- [12] P.J. Li, I. Kangasniemi, K. de Groot, T. Kokubo, *J. Am. Ceram. Soc.* **77**, 1307 (1994)
- [13] X.P. Wang, Y.Y. Chen, L.J. Xu, S.L. Xiao, F.T. Kong, K.D. Woo, *J. Mech. Behav. Biomed. Mater.* **4**, 2074 (2011)
- [14] Y.M. Wang, J.Y. Huang, T. Jiao, Y.T. Zhu, A.V. Hamza, *J. Mater. Sci.* **42**, 1751 (2007)
- [15] R.A. Nogueira, L.M.C. Pinto, A.C.D. Ângelo, A.P.R.A. Claro, C.R. Grandini, *Phys. Rev. B* **16**, 2746 (2013)
- [16] H.S. Kim, T.Y. Ra, I.D. Yeo, H.J. Bang, Y.G. Yoo, W.Y. Kim, *J. Mater. Sci. Technol.* **24**, 33 (2008)
- [17] Z. Evis, M. Usta, I. Kutbay, *Mater. Chem. Phys.* **110**, 68 (2008)
- [18] P.J. Li, *J. Biomed. Mater. Res. A* **66**, 79 (2003)
- [19] A. Arifin, A.B. Sulong, N. Muhamad, J. Syarif, M.I. Ramli, *Mater. Des.* **65**, 1028 (2015)
- [20] C.Q. Ning, Y. Zhou, *Acta Biomater.* **4**, 1944 (2008)
- [21] H.Z. Ye, X.Y. Liu, H.P. Hong, *J. Mater. Sci. Technol.* **29**, 523 (2013)
- [22] Q. Chang, H.Q. Ru, D.L. Chen, X.Y. Yue, L. Yu, C.P. Zhang, *J. Mater. Sci. Technol.* **27**, 546 (2011)
- [23] H.T. Anawati, H. Asoh, T. Ohno, M. Kubota, S. Ono, *Corros. Sci.* **70**, 212 (2013)
- [24] M. Yousefpour, A. Afshar, J.Y. Chen, X.D. Zhang, *Mater. Des.* **28**, 2154 (2007)