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CHARACTERIZATION OF THE GRADED MICROSTRUCTURE IN POWDER SINTERED POROUS TITANIUM

CHARAKTERYSTYKA GRADIENTOWEJ MIKROSTRUKTURY POROWATEGO TYTANU SPIEKANEGO Z PROSZKU

The proposed sintering process produce porosity and functional graded microstructure in the sinterd titanium powders. Titanium powders with different micro sizes were sintered at the proposed temperature region at 1200 and 1300°C for 2h. The apatite-forming on the graded microstructure is observed by immersion test in Hanks balanced salt soluion at 37°C. Sintering condition of titanium powders is estimated by thermogravimetry-differential thermal analysis (TG-DTA). The synthersied surface structures and apatite-forming ability were characterized by a field emission scanning electron microscopy (FE-SEM) observation and energy dispersive X-ray spectroscopy (EDS) analysis. As results, these graded microstructure of sintered porous titanium powders reveals apatite-forming ability as osseointegration by calcification in Hanks balanced salt soluion(HBSS) at 37°C.

Keywords: titanium, powder metallurgy, porous structure, sintering, biomaterial

1. Introduction

The characteristics of titanium (Ti) and its alloys are well known as lightweight, excellent corrosion resistance and high strength. These metallic materials are widely used in airplane, space shuttle, weapon, electrodes, insulating materials, heat exchangers, filters, membranes and biomaterials as the next generation materials. The most common biomedical metallic materials used today are titanium and its alloys in dental prosthesis and orthopedic implants [1-4]. Ni, Al, V, Cr and Co element also used as additional element for the altered functional properties in Ti-based alloys [5, 6]. Especially, Implant with a chemically composed of pure Ti can reduce a safety hazards form toxic potential elements in Ti-based alloys because it is desirable to avoid toxic element like Ni, Al and Cr.

Meanwhile, porous materials have advantaged properties for bone tissue engineering [7, 8]. Titanium and its alloys also have been attempted to develop porous materials as bio-materials due to excellent osseointegration between implant materials and bone tissue [9-11]. In addition, the controlled porosity can be solved the major problem of elastic modulus mismatch between bone tissue and metallic implant [12].

Recently, binder is used sintering of metallic powder in industrials goods due to this method makes mass production possible by metal injection molding as like engineering plastic production [13-15]. Ti powders also can be sinterd by binder mixing. Especially, the sintered titanium powders with highly

porosity are one of high potential as scaffold materials for orthopedic and dental application.

In this study, we aim to fabricate the sintered titanium powders by solution binder treatment. It has not yet been report for binder mixing of Ti powder in aqueous solution binder for implant.

Sintering process of titanium powders by binder solution streatment, its microstructure, characterization of mechanical properties and apatite formability in HBSS will be discussed in detail.

2. Experimental

The master Ti powders were prepared by blending pure Ti powders (purity 99.9%, 150µm, High Purity Chemicals, Japan) with two binders. These binders are 5 wt. % PVA (Polyvinyl alcohol (1500), Junsei Chemical Co., Ltd., Japan) solution and 5 wt. % PVA solution with the dispersion of carbon nanotubes (CNTs) 1g by gum arabic (GA) treatment. The mixing ratio of CNTs is 0.3g/g GA was added to 500ml of 5 wt. % PVA solution. And then, it was carried out mixing Ti powders and each binder solution to make two Ti powder mixtures at room temperature. The obtained powder slurries were dried under an oven-dryer at 100°C for 24hours in air.

These Ti powder mixtures were uniaxially pressed with a 230MPa into the disk-like green compact with a 30.0mm in diameter and a 3.0mm in thickness. The consolidated bulk pellet specimens were sintered at 375°C (1) for 1 hour, 495°C

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(2) for 1 hour and 1200°C (3) or 1300°C (4) for 2 hours in vacuum condition which are based on DTA result in Fig. 1. These isothermal heat treatments of specimens in Table 1 were carried out sintering process in a heating rate of 10°C/min with non-pressure.

TABLE 1
Experimental composition of the sintered Ti powders

Name	Composition (sintering temperature)
PVA1200	Ti + 5% PVA binder treatment (1200°C)
PVA1300	Ti + 5% PVA binder treatment at (1300°C)
CNT1200	Ti + 5% PVA + CNT + GA binder treatment (1200°C)
CNT1300	Ti + 5% PVA + CNT + GA binder treatment (1300°C)

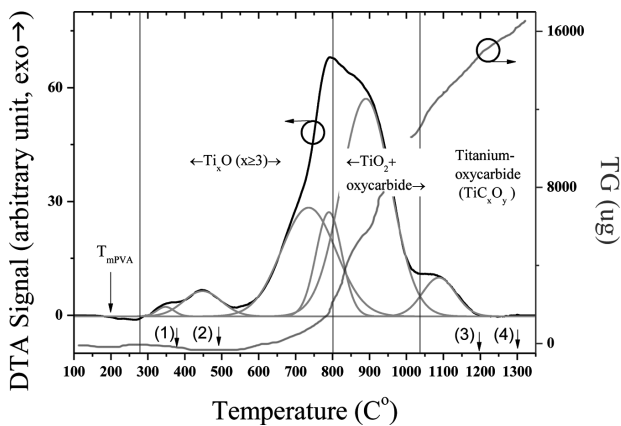


Fig. 1. DTA trace of the PVA treated Ti powder with a heating rate of 10°C/min

Mechanical properties of the sintered specimens were measured by using rectangular rods in Fig. 2. Uniaxial tensile and compressive tests were performed at room temperature by Instron type machine. The strain rate was used 0.1 and 0.01 mm/s in the gauge dimensions with 2.0×2.0×13.2 mm for tensile test and 2.5×2.5×5.0 mm for compressive test in Fig. 1. Fracture surface was observed with a field emission scanning electron microscopy (SEM: FE-SEM, TESCAN MIRA 3, Czech Republic).

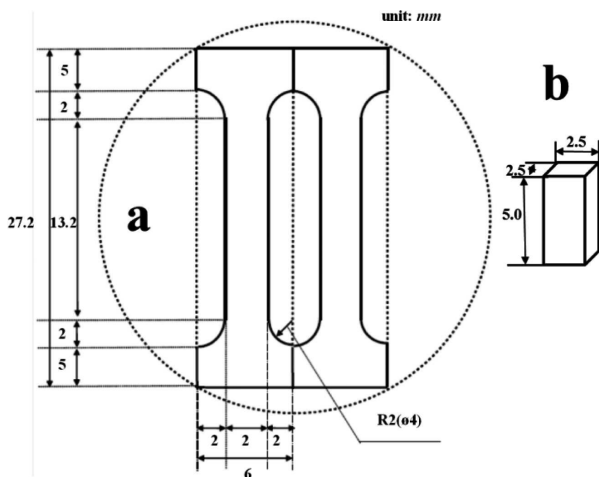


Fig. 2. Schematic illustration of the specimen types in tensile-test (a) and compressive-test (b)

The sintered specimens were immersed in 300 ml of Hank's balance salt solution (HBSS containing 0.186 g/l CaCl₂·2H₂O, 0.2 g/l MgSO₄·7H₂O, 8 g/l NaCl, 0.4 g/l KCl, 0.09 g/l Na₂HPO₄·7H₂O, 0.06 g/l KH₂PO₄, 0.35 g/l NaHCO₃, 1.0 g/l glucose) at 37°C for 5 days and 9 days. And then the second immersion was carried out in 300 ml of HBSS at 37°C for 7 days. After each immersion, all specimens were gently washed with distilled water and oven dried at 100°C for 24 hours in the air. Calcification was characterized by FE-SEM with energy dispersive X-ray analysis systems (EDS).

3. Results and discussion

Pore volume of the sintered specimens was estimated by Archimedes method. These porosity levels show around 25% with 24 μm~85 μm pore size. Fig. 3 shows stress-strain behavior of sintered porous Ti powders with two kind of binder treatment. Ultimate tensile strength (UTS) and fracture elongation of these specimens sintered at 1200°C and 1300°C are 50 MPa with 2.1% for PVA12, 118 MPa with 2.9% for PVA13, 41 MPa with 1.4% for CNT12 and 90 MPa with 2.0 for CNT13 specimen, respectively. UTS values and fracture elongation of PVA series show higher strength then those of CNT series.

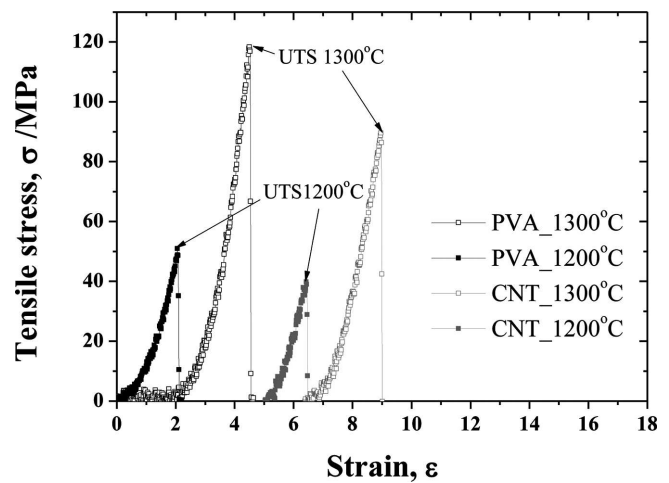


Fig. 3. Stress-strain curves of sintered specimens upon tensile test at 1200°C and 1300°C

Fig. 4 shows SEM fracture surface morphology of the sintered specimens at the planned temperatures and sintering condition of Ti powders. Consolidated powders in all specimens are still remained after tensile test. There are traces of transgranular fracture on surface of specimens. Fracture surface have order of magnitude difference in consolidated area. The sintered PVA and CNT specimens at 1300°C exhibit wide connecting areas which is compare with those of the sintered PVA and CNT specimens at 1200°C. This phenomenon has a direct relationship to tensile strength in Fig. 3.

Fig. 5 shows effect of strain rate in stress-strain curves of sintered specimens. Fig. 5a clearly exhibits the effect of different strain rate on the tensile behavior of the sintered Ti powders.

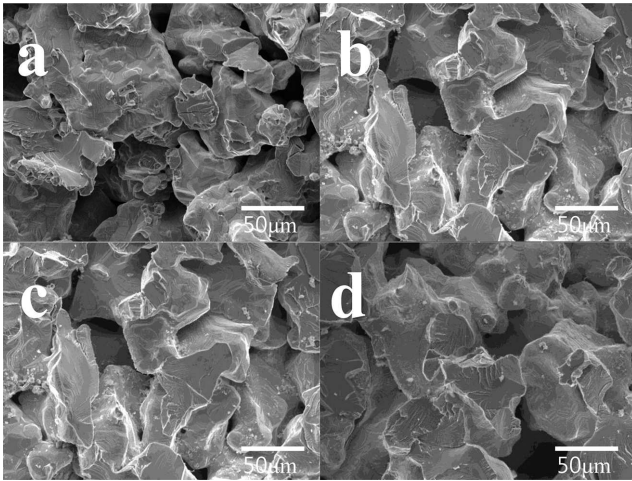


Fig. 4. Fracture surface by tensile test: (a) PVA 1200°C, (b) PVA 1200°C, (c) CNT 1200°C and (d) CNT 1300°C

PVA1300 and PVA 1300 are elastically tensioned until about 1.4% and 2.0% strain at both strain rates (0.1mm/s and 0.01mm/s), respectively. In case of strain rate with a 0.01mm/s, PVA1300 exhibits fracture behavior that is decrease of tensile strength (90 MPa) than strain rate with a 0.1mm/s for 118 MPa [16, 17]. On the other hand CNT1300 reveals strain rate with a 0.01mm/s made increase tensile strength (124 MPa) then strain rate with a 0.1mm/s for 90 MPa. Compressive behavior in Fig. 5b confirms this phenomenon has correlation between binder treatment and fracture behavior in this study. Compressive behaviors also show same fracture behavior. PVA binder treatment contributed to decrease tensile strength (780 MPa with 39% in elongation) in high speed strain rate and CNT binder treatment contributed to increase compressive strength (930 MPa with 54% in elongation) under low speed strain rate in this study.

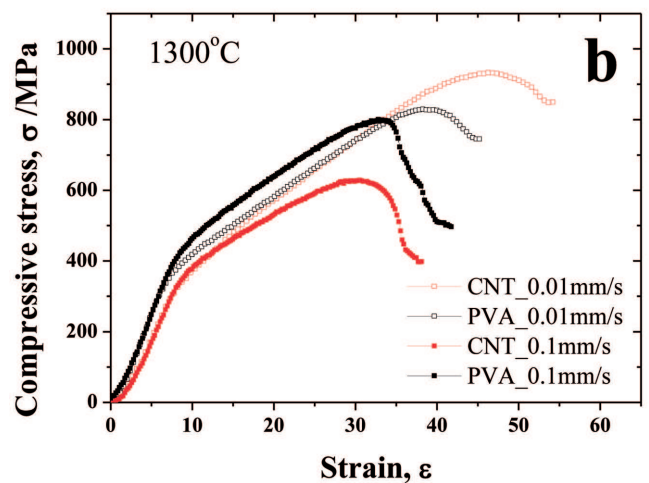
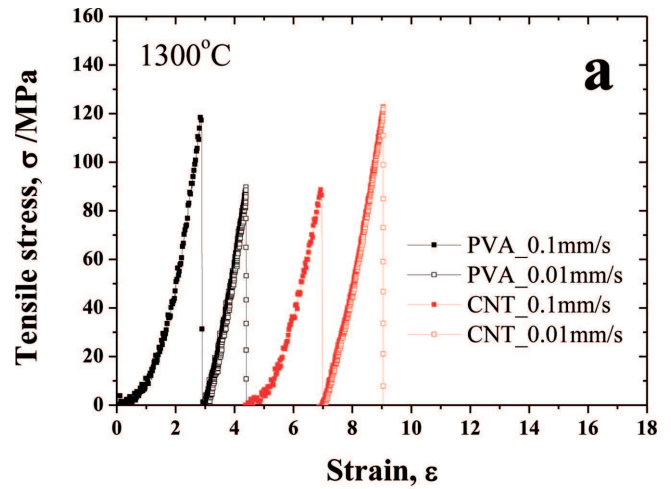


Fig. 5. Effect of strain rate in stress-strain curves of sintered specimens upon tensile test at 1300°C (a) and compressive test at 1300°C (b)

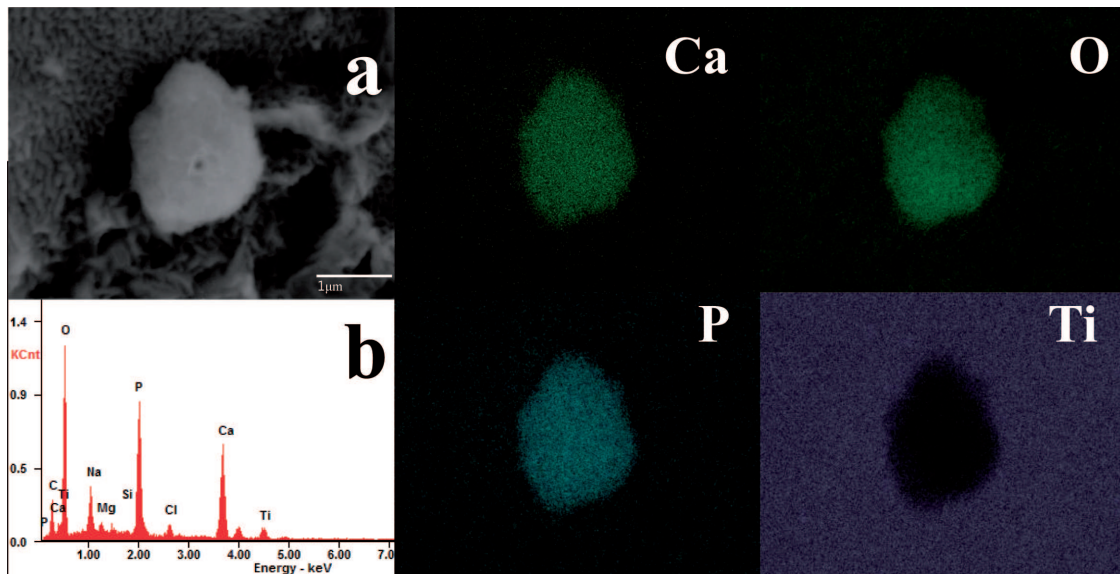


Fig. 6. Calcification analysis of the surface of sinterd Ti powder with PVA at 1300°C by soaking test in HBSS open to air at 37°C; (a) is immersed for 5 days at 37°C, (b) is EDS analysis result and Ca, O, P and Ti are mapping analysis results for (a)

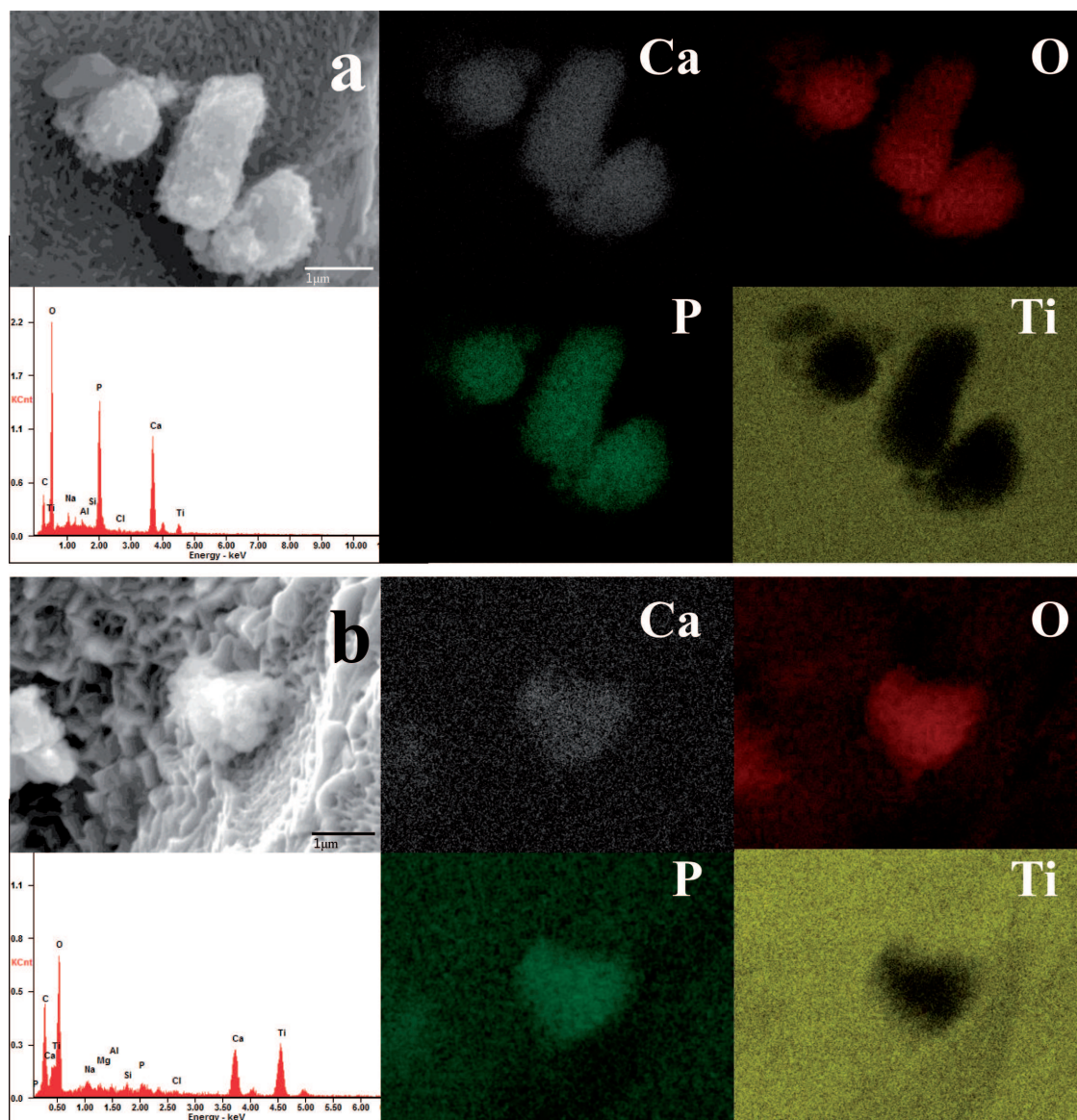


Fig. 7. Calcification analysis of the surface of sintered Ti powder with PVA(a) and CNT(b) at 1300°C by soaking test in HBSS open to air at 37°C; a and b are immersed for 9 days at 37°C, EDS analysis results for a and b, and Ca, O, P and Ti are mapping analysis results for (a) and (b)

In case of calcification, it has a strong relationship of osseointegration between implant and bone tissue. Osseointegration can be confirmed by calcification as bioactivity of these porous sintered Ti powder with binder treatment. Fig. 6 shows calcification behavior of the surface of PVA1300 specimen by soaking test in HBSS open to air at 37°C during 5 days. Fig. 6a exhibits apatite image on the surface of PVA1300. Existence of Ca and P composition estimated by Energy level peaks of EDS analysis result and mapping analysis results confirmed apatite formation by detection of Ca, O, P and Ti elements. EDS analysis result also shows process of apatite formation existence of sodium titanate crystals from detecting Na and Cl. It indicates substitution reaction from Na_2TiO_3 layer to CaTiO_3 layer in HBSS [18, 19].

Unfortunately, there is no certain trace of apatite formation in the surface CNT1300 as like a Fig. 6a in this study. Small quantity of Ca and P element, however, was widely detected on the surface of CNT1300.

Finally, Fig. 7 shows increase of calcification by growth apatite trace on the surface of PVA1300 and CNT1300 by soaking test in HBSS open to air at 37°C during 9 days. All EDS analysis results clearly exhibit apatite formation and growth by FE-SEM images and mapping analysis results for Ca, O, P and Ti element. The studied calcification on the surface of specimens in simulated body fluid, however, shows synthesis of titanium oxide nano-porous structure with Ca, O and P element, and the synthesized oxide layer is effective for apatite formation in this study.

4. Conclusions

In this study, we succeeded in fabricating multi-binding solution treatments and observation of mechanical properties of the graded microstructure in powder sintered porous as well as behaviour of calcification on the surface of these specimens. It summarizes as following:

1. PVA binder treatment is more effective method in sintering process of Ti powders.
2. CNT binder treatment show increase tensile and compressive strength under low speed strain rate.
3. PVA and CNT binder treated specimens in this study have bioactive surface that is confirmed apatite formation on the surface of specimens in HBSS.
4. Especially, the surface of PVA binder treated specimens revealed a good bioactivation for calcification after soaking in HBSS at 37°C.
5. To increase apatite formation on binder treated specimens in soaking HBSS, it needs to control the surface modification by C, Na and Cl element.

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REFERENCES

- [1] M. Long, H.J. Rack, *Biomaterials* **19**, 1621 (1998).
- [2] M. Niinomi, M. Nakai, T. Akahori, *Biomedical Materials* **2**, S167 (2007).
- [3] T. Akahori, Y. Oguchi, T. Hattori, T. Yasui, M. Fukumoto, H. Fukui, M. Niinomi, *Journal of the Japan Institute of Metals* **77**, 543 (2013).
- [4] J.-N. Gwak, S. Yang, J.-Y. Yun, J.-Y. Kim, S. Park, H.-S. Kim, Y.-J. Kim, Y.-H. Park, *Journal of Korean Powder Metallurgy Institute* **20**, 467 (2013).
- [5] J.J. Oak, A. Inoue, *Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing* **449**, 220 (2007).
- [6] J.J. Oak, D.V. Louzguine-Luzgin, A. Inoue, *Journal of Materials Research* **22**, 1346 (2007).
- [7] K. Rezwan, Q.Z. Chen, J.J. Blaker, A.R. Boccaccini, *Biomaterials* **27**, 3413 (2006).
- [8] J.R. Jones, P.D. Lee, L.L. Hench, *Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences* **364**, 263 (2006).
- [9] I.H. Oh, N. Nomura, N. Masahashi, S. Hanada, *Scripta Materialia*, **49**, 1197 (2003).
- [10] S.A. Yavari, S.M. Ahmadi, J. van der Stok, R. Wauthle, A.C. Riemsagel, M. Janssen, J. Schrooten, H. Weinans, A.A. Zadpoor, *Journal of the Mechanical Behavior of Biomedical Materials* **36**, 109 (2014).
- [11] S.R. Paital, N.B. Dahotre, *Biomedical Materials* **2**, 274 (2007).
- [12] C.E. Wen, Y. Yamada, K. Shimojima, Y. Chino, H. Hosokawa, M. Mabuchi, *Journal of Materials Research* **17**, 2633 (2002).
- [13] A. Arockiasamy, R.M. German, D.F. Heaney, P.T. Wang, M.F. Horstemeyer, R.L. King, B. Adcock, *Powder Metallurgy* **54**, 420 (2011).
- [14] R.M. German, *Materials* **6**, 3641 (2013).
- [15] H. Miura, *Journal of Korean Powder Metallurgy Institute* **20**, 323 (2013).
- [16] M. Guden, E. Celik, E. Akar, S. Cetiner, *Materials Characterization* **54**, 399 (2005).
- [17] K.T. Ramesh, *Metallurgical and Materials Transactions a-Physical Metallurgy and Materials Science* **33**, 927 (2002).
- [18] H.M. Kim, Y. Sasaki, J. Suzuki, S. Fujibayashi, T. Kokubo, T. Matsushita, T. Nakamura, *Bioceramics* **192-1**, 227 (2000).
- [19] H. Wang, E.S. Park, J.J. Oak, A.D. Setyawan, S.L. Zhu, T. Wada, X. M. Wang, A. Takeuchi, H. Kato, *Journal of Non-Crystalline Solids* **379**, 155 (2013).