Fabrication of Bioactive High Porous Hydroxyapatite Ceramics

[a*]Fatih Çalışkan, [a]Zafer Tatlı and [a]Ayça Sonkaya
[a]Sakarya University, Faculty of Technology, Department of Metallurgical and Materials Engineering, Sakarya University, 54187, Sakarya, Turkey

Abstract

The main subject of this study was to produce a net shaped micro porous hydroxyapatite ceramics. For this aim, initially fabrication of hydroxyapatite powder was achieved by a thermal extraction method which is inexpensive processing route. Phase determination of the yield of the process was carried out by X-ray diffraction method. Replica technique was used to produce a reticulated structure from hydroxyapatite powder. The foams were produced with various rates of additive as binder and additive-free compositions. After the HAp daubed on surfaces of substrate polymer was fired and sintered in the process at > 1100°C. The obtained ceramic foam was characterized using optical microscopy. The preform exhibited different pore sized structures depending binder rate and sintering temperature. As a result, hydroxyapatite preforms were produced with high porosity and their properties were improved by adding the binder which supports biocompability of HAp.

Keywords: Hydroxyapatite, bioactive ceramic, ceramic foam, replica method

Özet

Bu çalışmanın ana konusu, ağ yapılı mikro poroz hidroksiapatit seramiklerinin üretidir. Bu amaçla, ilk olarak hidroksiapatit tozu ekonomik bir üretim prosesi olan termal ekstraksiyon yöntemiyle üretilmiştir. Proses ürünündeki faz dönüşümü X-ray kırınımı metoduyla belirlenmiştir. Hidroksiapatit tozundan ağ yapılı gözenekli malzeme üretmek için Replika tekniği kullanılmıştır. Seramik köpükler, bağlayıcı olarak çeşitli oranlarda katkılar kullanarak veya katkısız kompozisyonlar kullanılarak üretilmiştir. Yüzeylerine HA sıvanmış altlık polimer yakılıp peşinden 1100°C üzerindeki sıcaklıklarda sinterlenmiştir. Elde edilen seramik köpükler optic mikroskopla karakterize edilmiştir. Preformlar, sinterleme sıcaklığı ve bağlayıcı oranına bağlı olarak farklı gözenek büyüklüklü yapılar ortaya koymuştur. Sonuç olarak, hidroksiapatit köpükler, yüksek poroziteli olark üretilmiş ve HAp biyoaktivitesini destekleyen bir bağlayıcı ilavesiyle özellikleri geliştirmiştir.

Anahtar Kelimeler: Hidroksiapatite, biyoaktif seramikler, seramik köpük, replica method

1. Introduction

Calcium phosphate-based hydroxyapatite (HA) ceramics used as a bioceramic material in medicine and dentistry are biocompatible due to very similar composition to that of the human bone [1-2]. HA has a significant potential of usage such as artificial bone of various prostheses constructions, cracks and broken bones in the repair and metallic biomaterials is used for coating [3-4]. The chemical structure of HA is mainly composed of Ca and P elements. These are the elements in the bones and teeth inorganic portion [5-6]. The material can be gained different features by adding the addition of many different ions into its structure. Bone-HA implant interface can be formed very strong bonds and bone is able to grow on this surface [7-8].

*Corresponding author: Address: Faculty of Technology, Department of Metallurgical and Materials Engineering Sakarya University, 54187, Sakarya TURKEY. E-mail address: fcaliskan@sakarya.edu.tr, Phone: +902642956501 Fax: +902642956424

After chemical precipitation methods were initially used to synthesize HA powder, its manufacturing was achieved by the water-based chemical deposition from solutions containing calcium and phosphate salts or by methods such as acid-base titration [4, 9-10]. However, because of these methods were complex and expensive, hydroxyapatite powder was produced by extraction of bovine bone in this study, which is both inexpensive and easy [11-12].

Hydroxyapatite ceramics are found various application areas such as implant coatings and filler for defects in the bone [3, 13]. Thus the changing demands can require HA products in different forms like particular form, spherical form powder and foam/preform. In addition to these, the most new application of porous ceramics is preform for polymer –matrix composites.

Different production methods are used for ceramics having porous structure [14–15]. These processing methods are generally classified into three groups: replica, sacrificial template and reaction techniques [16]. The replica method is one of the most attractive routes to fabricate the micro porous hydroxyapatite structures.

The aim of this study was the production of the micro porous hydroxyapatite for polymer matrix composite which is used in the human body. Hereby manufacturing of the uniform distributed and biocompatible hydroxyapatite reinforcement structure was successfully obtained.

2. Experimental

In this work, the fabrication of high porous HAp biocompatible ceramic foams was carried out. Initially, hydroxyapatite powder was fabricated from cow bone by thermal methods. This extraction started with crushing bones into small pieces, and continued with boiling up at 100°C for 3h on hot plate and burning up steps. As is given in Table 1, different types powders were used to produce hydroxyapatite preform. The produced HAp powder was analyzed by X-ray (Rigaku Dimaks 2200) for identifying its phase compositions.

Table 1. Codes and identifications used in the study

Code	***Identification***
PHA	Pure HAp
SHA	Sprey dried spherical HAp
MHA	Mixed HAp

The replica technique was used to fabricate microporous HAp foam for liquid polymer infiltration using polyurethane sponges. Submicron bentonite powder was used as binder. The bentonite addition allowed obtaining of near net shaped ceramic foams. When the bentonite daubed surface is dried, it protects former shape and gains strength due to highly plastic clay. In this study, the slurry was prepared to have approximately 50 wt% solid load. HAp powders with different bentonite ratios were mixed within pure water in ball milling for 4 h to prepare ceramic slurry. After slurry infiltration was completed and all polyurethane pore surfaces were covered with HAp mixtures. Firing process was took place at the temperatures till

500°C. All green structures were sintered at above 1100°C in a controlled atmosphere alumina tube furnace under Argon.

3. Results and Discussion

3.1: Phase Analysis of the HAp Powder

Figure 1 shows the X-ray analysis of the produced HAp powder. When handled Fig 1, it can readily be seen that all peaks belonged to $Ca_{10}(PO_4)_6(OH)_2$ phase. This means the final powder is HAp and the production was achieved with full transformation. There are no any impurity peaks in X-ray analysis.

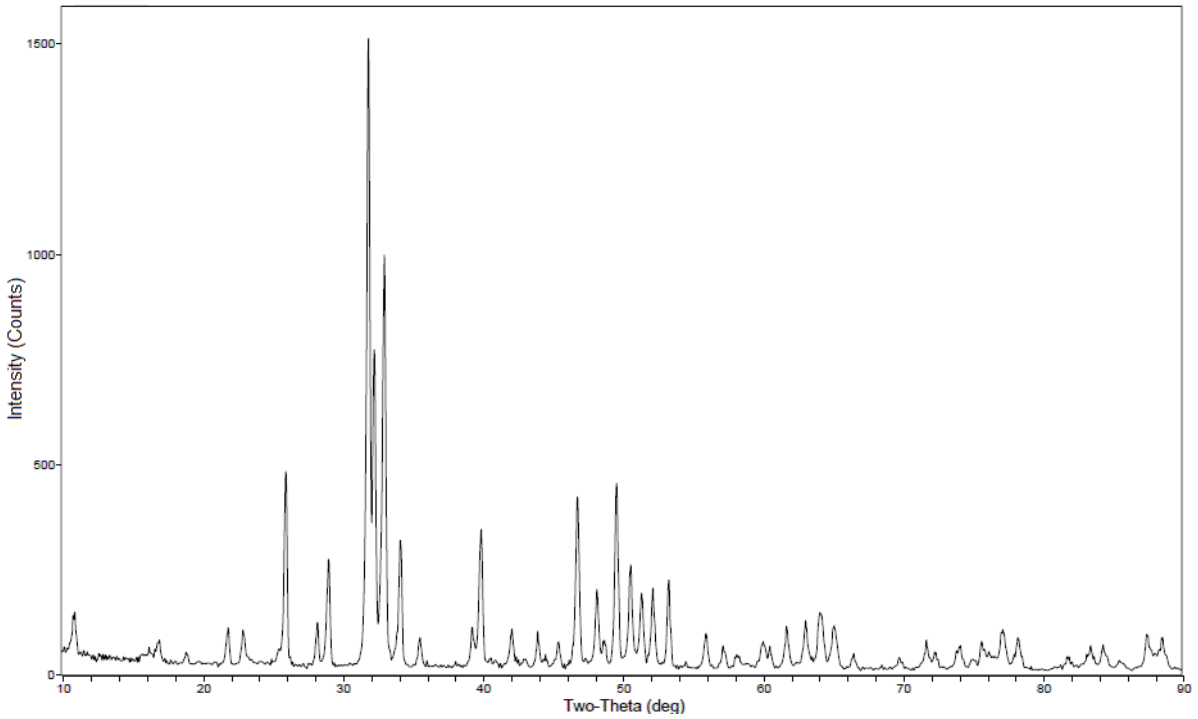


Figure 1. SEM micrograph of HAp powders

3.2. Fabrication of Hydroxyapatite Foams

Firstly, hydroxyapatite powder was used to obtain ceramic foams without any additive which was coded as PHA. HA Powder before use was sieved through a 300 mesh sieve screen. Even if the desired pore size provided, stiff and acceptable foam was not obtained even with increasing sintering temperature. The upper limit of sintering temperature is 1300°C. After this point, HAp starts to decompose and to transform tricalcium phosphate phase (TCP). Hence sintering without binder resulted with collapsing as seen in Fig 2.

Figure 2. The collapsed HAp foams

For this reason, the powder before use were planetary milled to get finer particles. Strength of HA foams increased by using finer particle size, but again strength values remained very low. While Fig 3a was belong to a foam from coarser powder (>30 micron), Fig 3b was made of finer powder (<10 micron). The main difference was pore size and more disconnected windows due to more shrinkage during the sintering process for the foam from finer powder. It can be easily attributed to finer particle size, which means higher surface area and more sinteractivity ability.

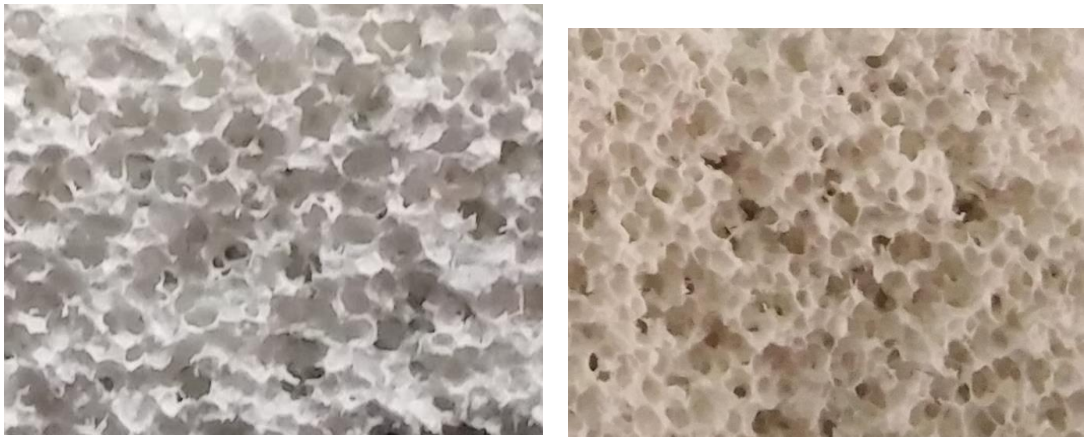


Figure 3. The reticulated structures of HAp prepared from a) finer powder b) coarser powder

The next step to increase the strength and to reveal effects of different powder morphology became was the use of spray dried spherical form powder. By this way, the authors tried to support skeleton of the preform. However the foam body didn't keep its shape and fell down as shown in Fig 4. That is to say, the desired result could not be obtained by this powder.

Figure 4. The collapsed HA foam produced from spray dried powder after sintering

Three different compositions were used to make ceramic foams and to compare the body which is the stiffer and more homogeneous porous. As is seen in Fig 5, stiffness and uniform pore distribution is as follows; MHA > PHA > SHA. The results are acceptable for binder-free process. Although MHA body had uniform pore size and distribution, it could collapse under slightly pressing.

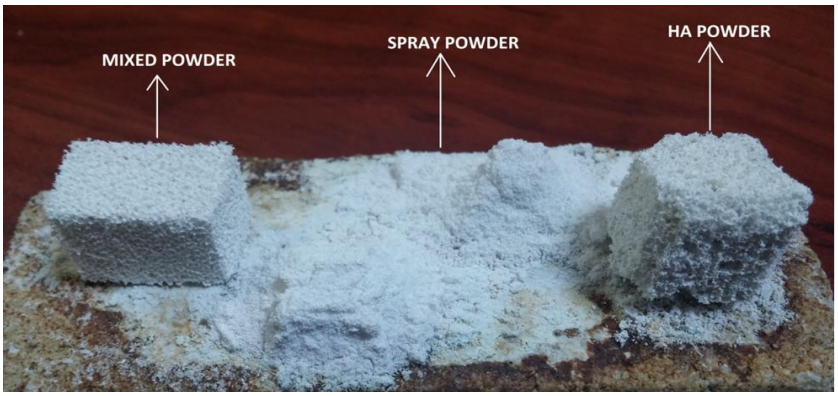


Figure 5. Preforms produced using different powder morphologies

Different temperatures were used for sintering of the HA replica. The sintering temperature exhibited an effect on pore size and shrinkage –densification rate of the body. Increase in temperature supported these behaviours, and differences being its results are clear between Fig 6a and Fig 6b.

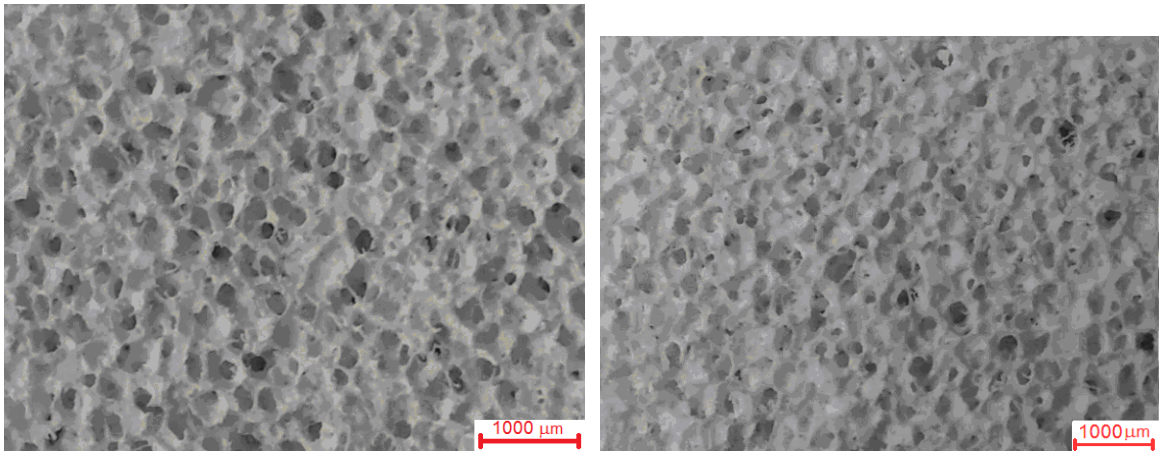
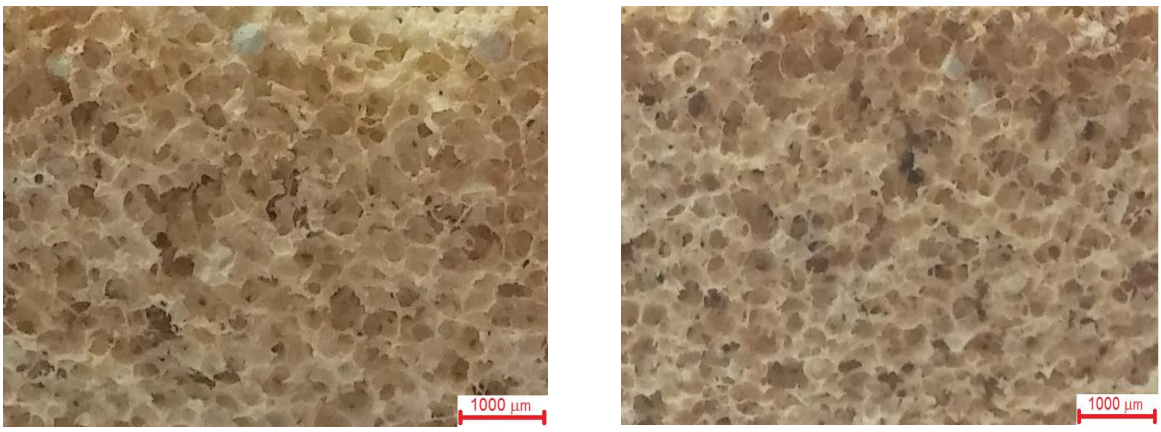


Figure 6. The ceramic foams produced at a) 1200°C b) 1250°C

The strength limitation problem for pure HA foams required a binder additive which was bentonite clay for this study. The bentonite was used to support stiffness in various rates 10%, 15% and 20%, respectively. Higher binder amount gave stronger bond for window. In addition, occupancy rate (solid/pore) in foam increased with the increasing binder amount. Fig 7c showed 20% bentonite rate could be excess because this bentonite content caused occurring of closed windows and improper structure for infiltration while Fig 7a and Fig 7b were acceptable for infiltration. A colour change in HA foam was observed with the increase in bentonite rate. As the bentonite content was increased, and the shrinkage cracks started to occur. A relation between bentonite rate and porosity percentage was shown in Fig 9. The increase of porosity percentage had opposite proportional relation to binder rate. This effect was due to the fact that bentonite additive strongly supported to densification and volumetric shrinkage.



(a) (b)

(c)

Figure 7. The effect of bentonite addition for **a)** 10% bentonite **b)** 15% bentonite **c)** 20% bentonite

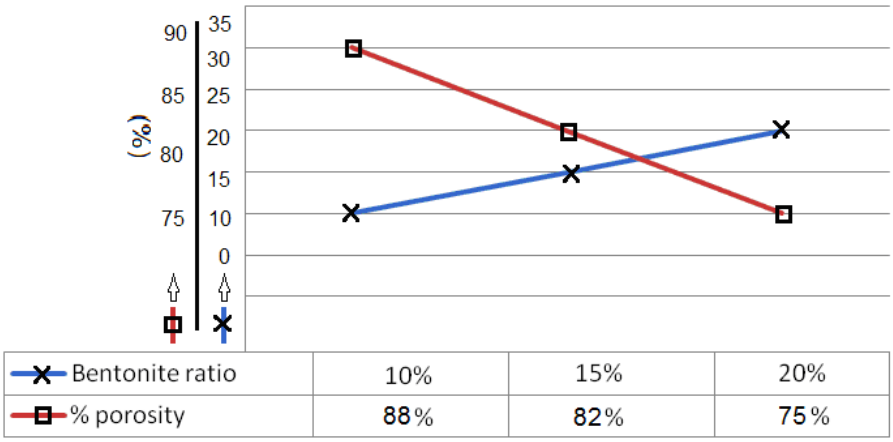


Figure 8. The relation of porosity and bentonite rate

Measurements of pore size and arm thickness were performed on Figure 9. While the mean thickness of arms of the window was approximately 150 microns, pore size was in the range of 250-450 micron.

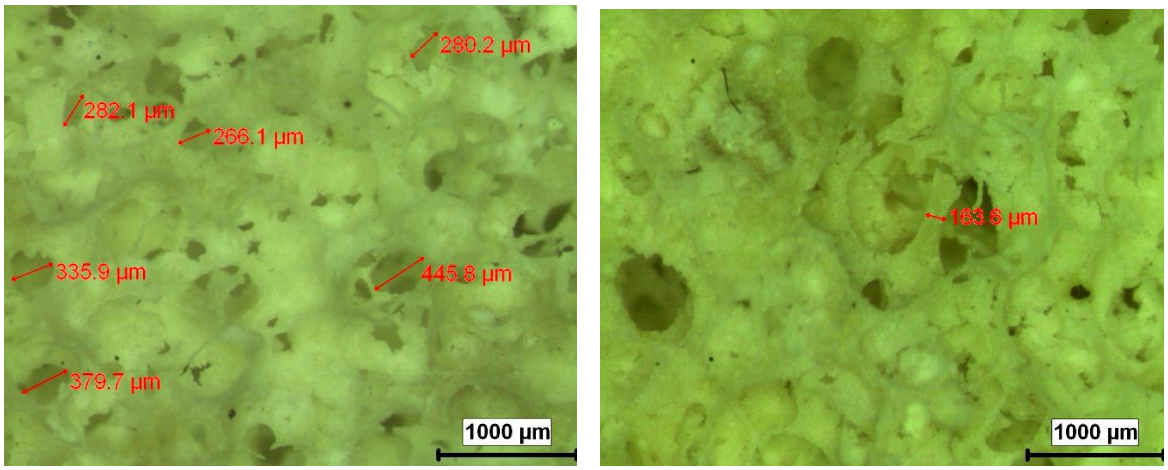


Figure 9. Pore size and arm thickness in the HA samples with 10% bentonite

4. Conclusion

As a result of this study, monophasic homemade hydroxyapatite powder from cow bone was produced by thermal method. Replica technique was used to obtain high porous HA preform. Pure HA, spray dried HA and the mixed HA mixtures were prepared to have a relatively strong HA foams. Due to insufficient strength of these, bentonite as a binder was used and significantly supported frame of porous structure. The optimum ratio of the binder was determined as 10 (wt. %). Finally the obtained ceramic foams had an application potential in implant area. Because besides being a bone substrate, it is a biocompatible uniform distributed and strong reticulated reinforcement for infiltration of liquid polymer to produce implant PMC materials.

ACKNOWLEDGEMENT

This study was financially supported by Sakarya University Commissions for Scientific Research Projects within the context of "BAP-2012-09-08-004" numbered project.

Reference

[1] Weng, W., and Baptista, J. L., A New Synthesis of Hydroxyapatite, Journal of the European Ceramic Society, 17, 1151-1156, 1997.
[2] Vallet-Regi M., Rodriguez-Lorenzo L.M., Salinas A.J., Synthesis and characterisation of calcium deficient apatite, Solid State Ionics 101-103 (1997) 1279-1285
[3] Sanden, B., Olerud, C., Petren-Mallmin, M., Larsson, S., 2002. Hydroxtapatite coating improves fixation of pedicle screws. The jour. of bone & joint surgery (Br), vol. 84-B: 387-391, 2002.
[4] Tas, A.C. Combustion synthesis of calcium phosphate bioceramics powders, Journal of the European Ceramic Society 20, 2389-2394, 2000.
[5] Nakamura, T., Bioceramics in Orthopedic Surgery. Bioceramics. 9, 31-34, 1996.
[6] Hench LL. Bioceramics: from concept to clinic. J Am Ceram Soc. 1991;74(7):1487–510.
[7] Tirrell, M., Kokkoli, E., The role of surface science in bioengineer materials, California, 2001.
[8] H.S. Ryua, K.S. Honga, J.K. Leeb, D.J. Kim, J. H. Leed, Chang B. S., Lee D.H., Lee C. K., Chung S. S., Magnesia-doped HA/b-TCPceramics and evaluation of their Biocompatibility, Biomaterials 25 (2004) 393–401
[9] Chen, F., Wang, Z.C. and Lin, C.J., Preparation and characterization of nano-sized hydroxyapatite particles and hydroxyapatite/chitosan nano-composite for use in biomedical materials. Materials Letters 57, 858-861, 2002.
[10] Feng, W., Li, M.S., Lu, Y.P. and Qi, Y.X., A simple sol-gel technique for preparing hydroxyapatite nanopowders. Materials Letters 59, 916-919, 2005.
[11] Vildan, W. M., Herliansyah M. K., Nuroho W. P. And Senjaya W., Characterization of sintered hydroxyapatite from bovine bone, Jurnal Mesin dan Industri, Vol 4, No 1, ISSN 1693-704X, Hal. 77-81, Januari 2007.
[12] Haberko K., Bucko M.M., Brzezinska M. J., Haberko, M., Mosgava, W., Panz,T., Pyda, A.,Natural Hydroxyapatite - Its
behaviour during heat treatment. J. Eur. Cer. Soc., 537-542, 2006.

[13] F. N. Oktar, G. Göller, Sintering effects on mechanical properties of glass-reinforced hydroxyapatite composites, Ceramics International 28, 617–621, 2002.
[14] A. Herzog, U. Vogt, O. Kaczmarek, R. Klingner, K. Richter, H. Thoemen, Porous SiC ceramics derived from tailored wood-based fiberboards. J. Am. Ceram. Soc. 89, 1499–1503 (2006)
[15] J.H. Eom, Y.W. Kim, I.H. Song, H.D. Kim, Processing and properties of polysiloxane-derived porous silicon carbide ceramics using hollow microspheres as templates. J. Eur. Ceram. Soc. 28, 1361–1364 (2008)
[16] Y.W. Kim, S.H. Kim, I.H. Song, H.D. Kim, C.B. Park, Fabrication of open-cell. Microcellular silicon carbide ceramics by carbothermal reduction. J. Am. Ceram. Soc. 88, 2949–2951 (2005)