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# Alumina–titania ceramics prepared by microwave sintering and conventional pressure-less sintering

Han-min Bian[a,c], Yong Yang[a,b,*], You Wang[a], Wei Tian[d], Hai-fu Jiang[e], Zhi-juan Hu[c], Wei-min Yu[c]

[a] *Department of Materials Science, Harbin Institute of Technology, Harbin, China*
[b] *School of Materials Science and Engineering, Hebei University of Technology, Tianjin, China*
[c] *Tianjin Cement Industry Design & Research Institute Co. Ltd., Tianjin, China*
[d] *China Gas Turbine Establishment, Chengdu, China*
[e] *National Defense Science and Technology Key Lab for Reliability and Environment Engineering Technology, Beijing Institute of Spacecraft Environment Engineering, Beijing, China*

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ABSTRACT

Nanostructured alumina–titania composite powders were used to prepare alumina–titania ceramics by microwave sintering and conventional pressure-less sintering. The effect of microwave sintering and conventional pressure-less sintering on densification, microstructure and properties of alumina–titania ceramics were evaluated. The results showed that the alumina–titania ceramic prepared by microwave sintering exhibited shorter sintering time, significantly enhanced densification, higher density, finer and more homogenous microstructure, higher strength, higher hardness and higher fracture toughness when compared with conventionally processed counterpart.

## 1. Introduction

Alumina–titania ceramic composite is a good ceramic material for many applications, e.g. gas separation, biomedical processes, support for transition metal catalyst, electronic and optical applications [1–5]. It was also reported that addition of titania to alumina considerably changed its sintering behaviour to manufacture dense ceramics [6,7]. In addition, the fracture toughness and wear resistance of alumina was improved with dispersion of titania [8,9].

On the other hand, many researches showed that grain refinement in alumina ceramics led to improved properties [10–14]. Fine-grained alumina matrix ceramics were considerably investigated and reported to possess superior properties compared to their conventional coarse-grained counterparts [15–17]. A number of techniques have been attempted to produce fine-grained alumina matrix ceramics, including hot pressing, hot isostatic pressing, spark plasma sintering, microwave sintering, thermal spraying, laser-based techniques, etc. [13]. Among the possible processes, microwave sintering (MWS) has received much attention in recent years [18–25]. Microwave processing is a distinctive and alternative technique when compared with the available processes utilizing the conventional heating sources. Owing to microwave–material molecular interaction, microwave heating is of internal and faster [20]. Microwave sintering results in improved quality of the product with time and energy savings compared with conventional sintering [22]. Processing of fine-grained alumina matrix ceramics via microwave sintering was highlighted also since the consolidation could be achieved at much lower temperatures [23].

However, to the best knowledge of authors, there were few reports on the preparation of alumina–titania ceramics by microwave sintering, and especially on the microstructure and properties of microwave sintered alumina–titania ceramics prepared from nanostructured composite powders.

In the present investigation, nanostructured alumina–titania composite powders were used to prepare alumina–titania ceramics by microwave sintering and conventional pressure-less sintering. The effect of microwave sintering and conventional pressure-less sintering on densification, microstructure and properties of alumina–titania ceramics were investigated in detail.

## 2. Materials and methods

Nanostructured alumina–titania composite powders with composition of 87 wt.% alumina and 13 wt.% titania were used to prepare alumina–titania ceramics. The nanostructured alumina–titania composite powders were powder mixture with alumina and titania mixing at a nanometer–nanometer level. The raw powders are $Al_2O_3$ (δ and γ phases, 99.9% grade, Degussa Co. Ltd., Germany) with a grain size of

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* Corresponding author at: School of Materials Science and Engineering, 433#, Harbin Institute of Technology, Harbin 150001, China. Tel.: +86 451 86402752; fax: +86 451 86413922.
*E-mail address:* hityangyong@163.com (Y. Yang).

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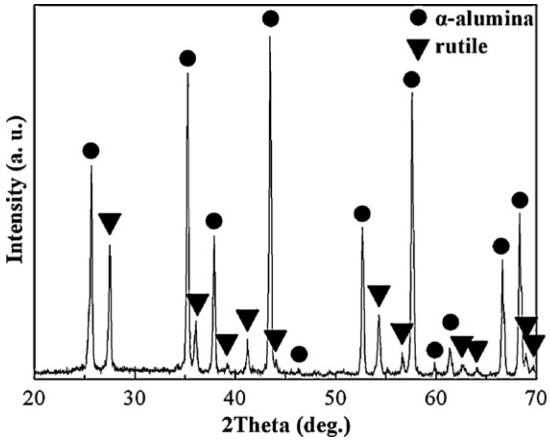

**Fig. 1.** XRD pattern of the nanostructured alumina–titania composite powders.

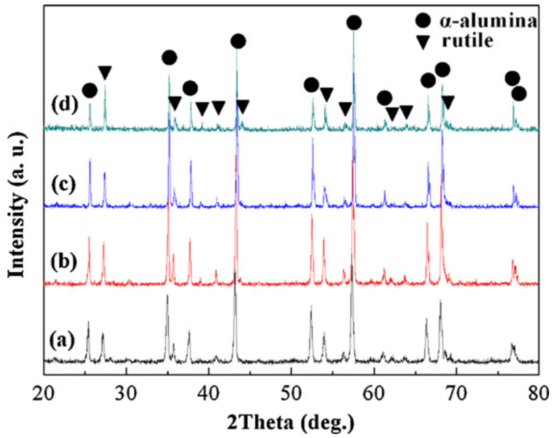

**Fig. 3.** XRD patterns of the alumina matrix ceramics prepared by microwave sintering and pressure-less sintering of the nanostructured alumina–titania composite powders: (a) PLS1250, (b) PLS1350, (c) PLS1450 and (d) MWS1250.

20–45 nm and $TiO_2$ (anatase, 99.9% grade, Nanjing High Technology of Nano Material Co. Ltd., China) with a grain size of 20–50 nm. The preparation process of the nanostructured alumina–titania composite powders included three stages: (1) raw powders mixing by wet ball milling, (2) spray drying of the slurry and (3) heat treatment of the nanostructured composite powders. Fig. 1 shows the XRD pattern of the nanostructured alumina–titania composite powders, which indicates the composite powders consisted of α-alumina and rutile. Fig. 2 shows the SEM micrographs of the nanostructured alumina–titania composite powders. After the above reconstitution processing, nanostructured spherical composite powders with particle size ranged from 10 to 50 μm in diameter had been obtained.

The powders were cold pressed uniaxially at 60 MPa into green compacts 40 mm in diameter and 5 mm in thickness, after that the green compacts were cool-isostatic pressed under 280 MPa. The green samples were then sintered in a microwave furnace (multimode cavity) at 2.45 GHz. SiC was selected as a microwave susceptor to assist heating and sintering of the green samples. The microwave sintering temperature was set at 1250 °C with a holding time of 10 min and an approximately heating rate of 100 °C/min. After the definite isothermal holding time, the samples were slowly cooled down to room temperature in the furnace. The cooling rate was about 10–15 °C/min. The as-prepared alumina–titania ceramics by microwave sintering were referred to MWS1250. On the other hand, the green samples were pressure-less sintered at 1250 °C, 1350 °C and 1450 °C for 1 h in air with the heating rate of 5 °C/min for comparison. The as-prepared alumina–titania ceramics by pressure-less sintering were referred to PLS1250, PLS1350 and PLS1450, respectively.

The density of the alumina–titania ceramics was determined using the Archimedes method with distilled water as immersion medium. The hardness was determined by a Vickers indenter with an indent load of 49 N using ten indents for each sample. Fracture toughness measurement was performed on single edge-notch beam specimens (SENB) with a span of 16 mm. Flexural strength measurement was performed on bar specimens (3 mm × 4 mm × 36 mm) using a three-point bend fixture with a span of 30 mm. At least six specimens were tested for research test condition. The phase constitution of the alumina–titania ceramics was determined by X-ray diffraction (D/max-γB, Rigaku, Japan). The microstructure of the alumina–titania ceramics was characterized by scanning electron microscope (SEM, Hitachi S-4700, Japan).

## 3. Results

### 3.1. Phase constitution of the alumina–titania ceramics prepared by microwave sintering and pressure-less sintering

The XRD patterns of the alumina–titania ceramics prepared by microwave sintering and pressure-less sintering of the nanostructured alumina–titania composite powders were shown in Fig. 3. The nanostructured alumina–titania composite powders consisted of α-alumina and rutile as shown in Fig. 1. It can be seen from Fig. 3 that all the alumina–titania ceramics prepared by microwave sintering and pressure-less sintering of the nanostructured alumina–titania composite powders were composed of α-alumina and rutile, which was the same as that of the composite powders. That indicated there was no phase transition occurring in the sintering process of ceramics, which would be advantageous to the densification of ceramics.

### 3.2. Microstructure of the alumina–titania ceramics by microwave sintering and pressure-less sintering

The nanostructured alumina–titania composite powders were pressure-less sintered to the maximum temperature of 1250 °C, 1350 °C and 1450 °C for 1 h, and which were sintered to 70.1%, 80.2% and 91.5% density, respectively (Table 1). The relative density of the as-prepared alumina–titania ceramics increased with increasing the sintering temperature from 1250 °C to 1450 °C. The maximum relative density of the alumina–titania ceramics prepared

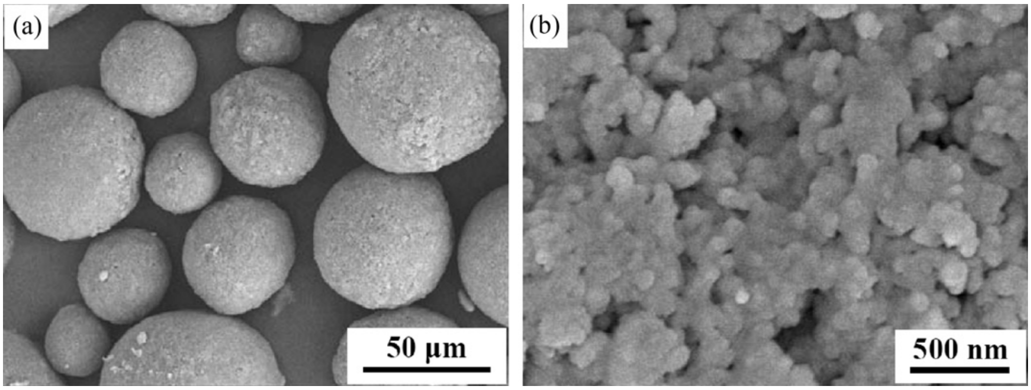

**Fig. 2.** SEM micrographs of the nanostructured alumina–titania composite powders: (a) overall SEM morphology and (b) high magnification SEM morphology of the particle surface showing the nano-sized grains.

**Table 1**
Properties of the alumina–titania ceramics prepared by microwave sintering and pressure-less sintering of the nanostructured alumina–titania composite powders.

| Ceramic | Relative density (%) | Flexural strength (MPa) | Vickers hardness (GPa) | Fracture toughness (MPa m$^{1/2}$) |
|---|---|---|---|---|
| PLS1250 | 70.1 | 69.3 ± 15.9 | 0.81 ± 0.15 | 0.79 ± 0.21 |
| PLS1350 | 80.2 | 239.4 ± 25.1 | 5.96 ± 0.24 | 1.74 ± 0.15 |
| PLS1450 | 91.5 | 362.6 ± 34.4 | 7.77 ± 0.33 | 3.64 ± 0.24 |
| MWS1250 | 98.1 | 576.8 ± 23.1 | 17.5 ± 0.6 | 4.11 ± 0.36 |

by pressure-less sintering was 91.5% in the sintering temperature range of 1250–1450 °C, which meant the alumina–titania ceramics were not fully densified. However, when the nanostructured alumina–titania composite powders were microwave sintered to the maximum temperature of 1250 °C for 10 min, which were sintered to 98.1% density (Table 1). That indicated the alumina–titania ceramics had been nearly fully densified by microwave sintering at 1250 °C for 10 min.

The SEM micrographs of the alumina–titania ceramics prepared by microwave sintering and pressure-less sintering were shown in Fig. 4. There was obvious microstructure difference for the alumina–titania ceramics prepared by microwave sintering and pressure-less sintering. The grains shape of PLS1250 ceramic was still spherical. There was a little grain growth for PLS1250 ceramic compared with the composite powders (Figs. 4a and 1b). Grain size of the spherical grains in PLS1250 ceramic was in the range of 200–300 nm. Although the grain boundary had formed, there were a large number of pores forming pore network in PLS1250 ceramic. The microstructure of PLS1250 ceramic was porous. More mass transfer between grains of PLS1350 ceramic occurred than that of PLS1250 ceramic (Fig. 4b and a), and many grains coalesced into irregular blocky grains. But the mass transfer of PLS1350 ceramic was still insufficient and there were also many pores between grains. The grain size of PLS1350 ceramic increased to 300–400 nm. The grains of PLS1450 ceramic grew evidently compared with that of PLS1350 ceramic. There were large equiaxed grains formed in PLS1450 ceramic because of coalescent of fine grains (Fig. 4c). Although the pores in PLS1450 ceramic was reduced compared with that of PLS1350 ceramic, there were still some big pores retained in PLS1450 ceramic. The relative density of PLS1450 ceramic was 91.5%, which indicated the alumina–titania ceramics were still not fully densified despite pressure-less sintered to 1450 °C. However, when the nanostructured alumina–titania composite powders were microwave sintered to 1250 °C for 10 min, MWS1250 ceramic was quite dense. Although there was a little grain growth for MWS1250 ceramic compared to the composite powders, the microstructure of MWS1250 ceramic was much finer (Fig. 4d). That indicated dense fine-grained alumina–titania ceramic had been obtained after microwave sintering at 1250 °C for 10 min. The higher density and finer microstructure of MWS1250 ceramic compared with that of the PLS1250, PLS1350 and PLS1450 ceramics were attributed to the use of the superior microwave sintering method, which will be discussed later.

### 3.3. Mechanical properties of the alumina–titania ceramics by microwave sintering and pressure-less sintering

Table 1 showed the properties of the alumina–titania ceramics prepared by microwave sintering and pressure-less sintering of the nanostructured alumina–titania composite powders. The mechanical properties of MWS1250 ceramic were much higher than that of PLS ceramics, e.g. the flexural strength, Vickers hardness and fracture toughness of MWS1250 ceramic were 59.1%, 125.2% and 12.9% higher than that of PLS1450 ceramic, respectively.

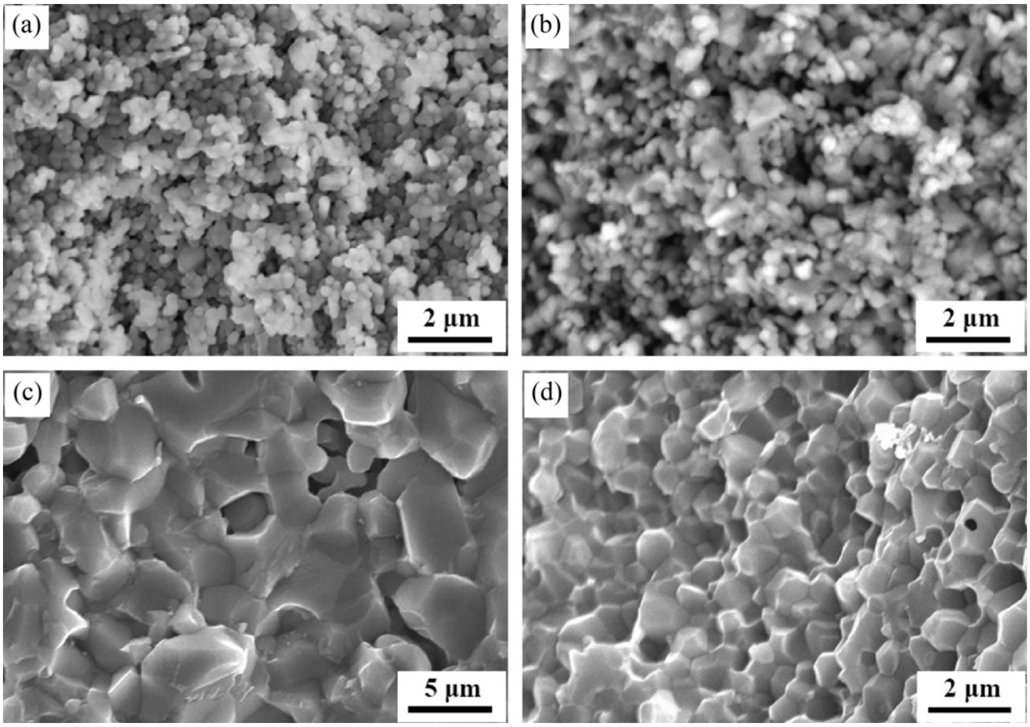

**Fig. 4.** SEM micrographs of the alumina–titania ceramics prepared by microwave sintering and pressure-less sintering of the nanostructured alumina–titania composite powders: (a) PLS1250, (b) PLS1350, (c) PLS1450 and (d) MWS1250.

It is known that the flexural strength of ceramics increases with increasing of the ceramics' relative density [26]. MWS1250 ceramic was much denser than PLS ceramics (Table 1). Therefore, the flexural strength of MWS1250 ceramic was higher than that of PLS ceramics. In addition, there is an empirical relation between strength and grain size in ceramics. The smaller the grain size is, the stronger the ceramic becomes. The grain size of MWS1250 ceramic was much finer than that of PLS1450 ceramic. Therefore, the flexural strength of MWS1250 ceramic was higher than that of PLS1450 ceramic.

The hardness of ceramics increases with increasing of the ceramics' relative density, and decreases with increasing of the ceramics' grain size. MWS1250 ceramic was much denser and finer than PLS1450 ceramic. Therefore, the Vickers hardness of MWS1250 ceramic was higher than that of PLS1450 ceramic.

In the present investigation, the fracture toughness of the alumina–titania ceramics was mainly determined by the relative density of the ceramics due to the big difference of the relative density between PLS ceramics and MWS1250 ceramic (70.1%, 80.2%, 91.5% and 98.1%, respectively). MWS1250 ceramic was much denser than PLS ceramics. Therefore, the fracture toughness of MWS1250 ceramic was higher than that of PLS ceramics.

Overall, the improved mechanical properties of MWS1250 ceramic compared with that of PLS ceramics were attributed to the enhanced densification and the finer and more homogeneous microstructure through the use of the microwave sintering method.

## 4. Discussion

The results obtained in the present study indicate that microwave sintering is a great potential and time-saving method for fabricating alumina–titania ceramics with uniform microstructure, which could influence the microstructure and thereby improve the mechanical properties comparing with the conventional pressure-less sintering.

As observed above, in comparison to the conventional pressure-less sintering, microwave sintering of alumina–titania ceramics to fully densification can be achieved at lower sintering temperature (1250 °C) and shorter sintering time (10 min). A temperature decrease of at least 200 °C was observed in microwave sintering as compared to conventional sintering for reaching fully densification (>98% theoretical), and at the same time, microwave sintering required at least 83% less processing time than required by conventional sintering, and similar observations on other materials have previously been reported by other researchers [13,27]. In addition, the Vickers hardness, flexural strength and fracture toughness of MWS1250 ceramic are higher than those of the conventionally fabricated alumina–titania ceramics (Table 1), which should be due to better densification of MWS1250 ceramic.

Solid state sintering is a diffusion controlled process with different modes, e.g. volume diffusion, grain boundary diffusion, and surface diffusion [24]. As for ceramics, the diffusing species are anions and cations. Microwaves, known as high frequency electromagnetic waves, were reported to interact with such ionic species and induce their motion [28]. This induced motion was resisted due to frictional, elastic and inertial forces. The electric field associated with the microwave radiation was attenuated and caused volumetric heating of the material due to the above resistance. Microwave field generates oscillation of free electrons and ions at high frequency resulting rapid volumetric heating of material through thermal agitation [13]. Comparing with conventional pressure-less sintering, microwave sintering requires less time due to volumetric heating. On the other hand, because microwave sintering is a non-contact technique, the heat is transferred to the material via electromagnetic waves and large amounts of heat can be transferred to material's interior, minimizing the effects of differential heating sintering [29]. High frequency magnetic field develops heat source within the specimen resulting preferential heating of porous regions with assisted material flow along interfaces. Thermal conduction transfers the radiation energy from surface to core by producing extreme thermal gradients, whereas microwave heating excites every crystal lattice resulting uniform distribution (or volumetric heating) of ceramic body. Hence, microwave sintering leads to rapid heating with reduced thermal stresses and higher heating efficiency. The reported "microwave effect" augmented the kinetics of synthesis and sintering reactions by 2 or 3 orders of magnitude or even more when conventional heating is substituted for microwave radiation [30]. For the above reasons, the MWS1250 ceramic microwave sintered at 1250 °C for 10 min showed better densification, higher density and certainly higher strength, hardness and fracture toughness than alumina–titania ceramics conventionally sintered for 1 h at the same temperature and even higher temperatures.

## 5. Conclusion

Alumina–titania ceramics were prepared by microwave sintering (MWS) and conventional pressure-less sintering (PLS) from nanostructured alumina–titania composite powders. There was obvious microstructure difference for the alumina–titania ceramics prepared by MWS and PLS. The microstructure of PLS alumina–titania ceramics were porous. The MWS alumina–titania ceramic, however, exhibited denser, finer and more homogenous microstructure compared with that of the PLS alumina–titania ceramics, which were attributed to the characteristics of rapid heating and volumetric heating of the superior microwave sintering method. The mechanical properties of the MWS alumina–titania ceramic were, therefore, much higher than that of the PLS alumina–titania ceramics, e.g. the flexural strength, Vickers hardness and fracture toughness of MWS1250 ceramic were 59.1%, 125.2% and 12.9% higher than that of PLS1450 ceramic, respectively.

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## References

[1] Q. Xu, M.A. Anderson, J. Mater. Res. 6 (1991) 1073–1080.
[2] M.A. Anderson, M.J. Gieselmann, Q. Xu, J. Membr. Sci. 39 (1988) 243–258.
[3] G.S. Walker, E. Williams, A.K. Bhattacharya, J. Mater. Sci. 32 (1997) 5583–5592.
[4] S.A. Jansen, S.A. Grabatia, N.M. Buecheler, Mater. Res. Soc. Symp. Proc. 291 (1993) 227–232.
[5] T. Kolodiazhnyia, G. Anninob, M. Spreitzerc, T. Taniguchia, R. Freerd, F. Azoughd, A. Panarielloe, W. Fitzpatricke, Acta Mater. 57 (2009) 3402–3409.
[6] T. Hernandez, M.C. Bautista, J. Eur. Ceram. Soc. 25 (2005) 663–672.
[7] S. Taruta, Y. Itou, N. Takasugawa, K. Okada, N. Otsuka, J. Am. Ceram. Soc. 80 (1997) 551–556.
[8] S.W. Lee, C. Morillo, J. Lira-Olivares, S.H. Kim, T. Sekino, K. Niihara, B.J. Hockey, Wear 255 (2003) 1040–1044.
[9] Y. Yang, Y. Wang, Z. Wang, G. Liu, W. Tian, Mater. Sci. Eng. A 490 (2008) 457–464.
[10] M.A. Meyers, A. Mishra, D.J. Benson, Prog. Mater. Sci. 51 (2006) 427–456.
[11] A. Mukhopadhyay, B. Basu, Int. Mater. Rev. 52 (2007) 257–288.
[12] V. Somani, S.J. Kalita, J. Am. Ceram. Soc. 90 (2007) 2372–2378.
[13] V. Viswanathan, T. Laha, K. Balani, A. Agarwal, S. Seal, Mater. Sci. Eng. R 54 (2006) 121–285.
[14] M. Aminzare, M. Mazaheri, F. Golestani-fard, H.R. Rezaie, R. Ajeian, Ceram. Int. 37 (2011) 9–14.
[15] P. Bansal, N.P. Padture, A. Vasiliev, Acta Mater. 51 (2003) 2959–2970.
[16] Y. Yang, D. Yan, Y. Dong, L. Wang, X. Chen, J. Zhang, J. He, X. Li, J. Alloys Compd. 509 (2011) L90–L94.
[17] Y. Yang, Y. Wang, W. Tian, Y. Zhao, J. He, J. Alloys Compd. 481 (2009) 858–862.

[18] R. Roy, D. Agrawal, J. Cheng, S. Gedevanishvilli, Nature 399 (1999) 668–670.
[19] T. Ebadzadeh, J. Alloys Compd. 489 (2010) 125–129.
[20] K. Tahmasebi, M.H. Paydar, J. Alloys Compd. 509 (2011) 1192–1196.
[21] K. Saitou, Scripta Mater. 54 (2006) 875–879.
[22] M. Oghbaei, O. Mirzaee, J. Alloys Compd. 494 (2010) 175–189.
[23] G. Golkar, S.M. Zebarjad, J.V. Khaki, J. Alloys Compd. 504 (2010) 566–572.
[24] S. Bose, S. Dasgupta, S. Tarafder, A. Bandyopadhyay, Acta Biomater. 6 (2010) 3782–3790.
[25] D. Demirskyi, D. Agrawal, A. Ragulya, J. Alloys Compd. 509 (2011) 1790–1795.
[26] R.L. Coble, W.D. Kingery, J. Am. Ceram. Soc. 39 (1956) 377–385.
[27] A. Mondal, A. Upadhyaya, D. Agrawal, Mater. Sci. Eng. A 527 (2010) 6870–6878.
[28] S.A. Freeman, J.H. Booske, R.F. Cooper, Phys. Rev. Lett. 74 (1995) 2042–2045.
[29] P.M. Souto, R.R. Menezes, R.H.G.A. Kiminami, Ceram. Int. 37 (2011) 241–248.
[30] R.R. Menezes, R.H.G.A. Kiminami, J. Mater. Process. Technol. 203 (2008) 513–517.