

Mechanical Properties and Crystallization Behavior of Silica-Based Ceramic Cores with Different Particle Morphologies

JeongSoo Park^{a,b}, Jeong-Gu Yeo^{a,*}, SeungCheol Yang^c and Churl-Hee Cho^{b,*}

^aEnergy Efficiency and Materials Research Division, Korea Institute of Energy Research, 152 Gajeong-ro, Yuseong-gu, Daejeon 34129, Korea

^bGraduate School of Energy Science and Technology, Chungnam University, 99 Daehak-ro, Yuseong-gu, Daejeon 34134, Korea

^cJeju Global Research Center, Korea Institute of Energy Research, 200 Haemajihae-ro, Gujwa-eup, Jeju, Jeju-do 63357, Korea

Herein, we investigate the influence of silica particle morphology on the mechanical properties and crystallization of ceramic cores, showing that the above factor influences the mixing, flow, and sintering (1200 °C, 12 h) behavior of feedstock. Ceramic cores were fabricated using angular and spherical silica particles, and their performance was evaluated by feedstock viscosity, flexural strength, shrinkage, apparent porosity, X-ray diffraction, and scanning electron microscopy analyses. The above analyses revealed that cristobalite was readily formed on spherical particles, and the corresponding core exhibited lower viscosity, improved flexural strength (1.7-fold) and reduced shrinkage (by as much as 15%) compared to those of the core comprising angular particles.

Key words: Ceramic core, Fused silica, Particle morphology, Strength.

Introduction

In investment casting, ceramic cores are utilized for casting small complex channels within gas turbine engine components to allow the passage of cooling air [1]. In this regard, the extremely low coefficient of thermal expansion ($0.5 \times 10^{-6} \text{ K}^{-1}$), excellent thermal shock resistance, chemical inertness, good stability in alkali solutions, and high melting temperature (as high as 1750 °C) of fused silica make the corresponding ceramics promising matrix materials [2]. In addition, the mechanical strength of most cores is improved by the incorporation of zircon [3].

A previous study addressed the effects of SiC addition on the thermomechanical properties of silica cores [4], showing that their mechanical strength and dimensional stability were closely related to the properties and nature of starting materials. Herein, we prepared ceramic formulations using silica with different particle morphologies but identical particle size, demonstrating that feedstock mixing, flow, debinding, and sintering behavior were influenced by particle morphology. Although high feedstock strength might be advantageous, high solid loadings commonly cause a steep rise of viscosity and thus lead to inhomogeneity. Thus, German reported that the viscosity of a given feedstock can be used to assess its homogeneity [5], with the highest solid loadings achieved at the lowest

possible viscosities. In another study, spherical alumina particles were shown to be advantageous for increasing the solid loading and sinterability [6]. Generally, high solid loadings increase the number of neighboring particle contacts and ensure density and dimension stability. In silica-based systems, fused silica readily undergoes crystallization during high-temperature sintering, resulting in the formation of a cristobalite phase that may cause mechanical strength reduction. In a previous investigation, the formation of cristobalite was inhibited by sintering temperature control [7]. However, in contrast to the abovementioned results, another study reported that appropriate loadings (10–20 wt%) of cristobalite improve ceramic core performance [8]. When cristobalite is used in combination with fused silica, their powder mixture accelerates crystallization and minimizes thermal expansion in the cast [9], i.e., in the absence of cristobalite, the excessive expansion of molten metal creates stress centers and results in premature failure.

Cristobalite has two polymorphs, namely α -cristobalite (stable below 230 °C) and β -cristobalite (stable above 230 °C), with the α - to β -cristobalite phase transition being accompanied by volumetric change, since the above phases exhibit octahedral structures with tetragonal and isometric symmetries.

Materials and Methods

Commercially available fused silica and zircon were used as raw materials, with their specific compositions and particle sizes listed in Table 1. Samples of angular

*Corresponding author:

Tel : +82-42-860-3744, 82-42-821-8606

Fax: +82-42-860-3133, 82-42-821-8839

E-mail: jgyeo@kier.re.kr, choch@cnu.ac.kr

Table 1. Characteristics of the raw powders for silica based ceramic core.

Sample	Type	Material	Specification	Company (Country)
K1	Angular	Fused Silica	325mesh 99.7% purity	Tecosil (United States)
	Angular	Zircon	1.0 μm 97.5% purity	Cenotech (Republic of Korea)
K2	Spherical	Fused Silica	325mesh 99.7% purity	Tecosil (United States)
	Angular	Zircon	1.0 μm 97.5% purity	Cenotech (Republic of Korea)

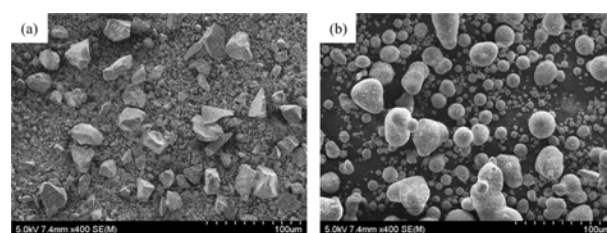
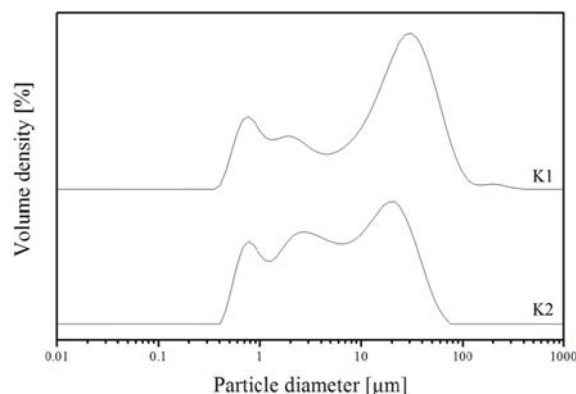
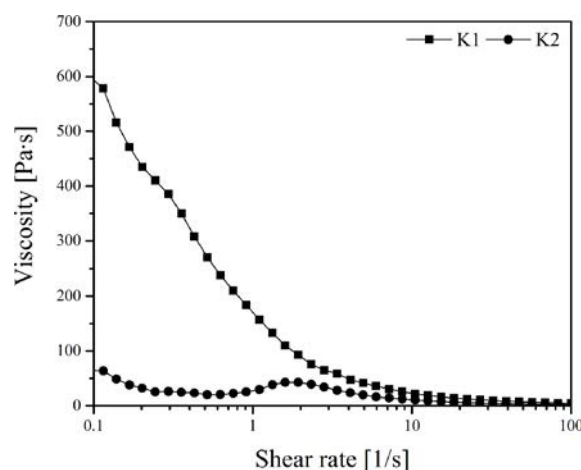
and spherical silica particles were denoted as K1 and K2, respectively, and zircon (comprising angular particles) was added to both samples. Both zircon and thermoplastic binders used in this study were identical to those used previously [4, 7]. All ceramic powder materials and binders were used as received. Ceramic powder mixtures comprised fused silica and zircon in a mass ratio of 3:1. The volumetric content of ceramics in the feedstock was fixed at 70% for subsequent injection molding.

To ensure uniform mixing, fused silica and zircon powders were ball-milled at room temperature for 6 h using zirconia balls, and the thus obtained powder was mixed with the thermoplastic binder at 1000 rpm at 80 °C for 12 h. For mechanical property measurements, the feedstock was formed into rectangular specimens ($6 \times 8 \times 90 \text{ mm}^3$) according to ASTM C1161-13 [10]. Thermal debinding of the prepared specimens was performed at 300 °C for 1 h at a heating rate of 0.2 °C min^{-1} and was followed by 12-h sintering at 1200 °C at a heating rate of 2.0 °C min^{-1} .

A universal testing machine (Model H5KT, Tinius-Olsen Inc., PA, USA) was used to measure three-point flexural strength at a crosshead speed of 1 mm min^{-1} and a span size of 80 mm. Linear shrinkage was calculated from the heating-induced length change of specimens. Microstructural characterization was performed by field emission scanning electron microscopy (FE-SEM; S-4800, Hitachi, Japan), and X-ray diffraction (XRD; D/MAX-2000, Rigaku, Japan) was used to investigate the phase transformations of ceramic cores. A particle size analyzer (Mastersizer 3000, Malvern Instruments Ltd., UK) was used to determine particle size distributions and specific surface areas of powder mixtures. A rheometer (MCR 501, Anton-Paar Ltd., Austria) was used to analyze feedstock viscosity.

Results and Discussion

Fig. 1 shows SEM images of K1 and K2 particles, revealing that the former ones were irregularly shaped and had sizes of $\sim 20\text{--}40 \mu\text{m}$. A large fraction of K2

**Fig. 1.** Scanning electron microscope image of (a) angular and (b) spherical raw silica material.**Fig. 2.** Particle size distribution of K1 and K2 powder mixture.**Fig. 3.** Viscosity dependence on shear rate of K1 and K2 feedstock.

particles were below 20 μm in size, with their concomitantly observed elongated agglomerates being not larger than 100 μm . Thus, K2 particles exhibited a tighter size distribution than K1 ones, as confirmed by laser scattering analysis (Fig. 2). The above analysis revealed that both samples showed trimodal particle size distributions that were similar in the region of $< 100 \mu\text{m}$. The mean diameters of K1 and K2 particles were determined as 30.2 and 12.2 μm , respectively, i.e., the K2 batch contained much finer particles. Moreover, the obtained particle size distributions were used to calculate the specific surface area of powder mixtures based on the assumption that all particles were spherical and nonporous. Importantly, the laser scattering method allows surface area measurement of coarse powders

containing particles of $\sim 3\text{--}200\ \mu\text{m}$ [11]. The surface area of K2 ($711\ \text{m}^2\ \text{kg}^{-1}$) exceeded that of K1 ($459\ \text{m}^2\ \text{kg}^{-1}$), implying that the former batch exhibited greater sinterability due to containing finer particles with higher specific surface areas.

Fig. 3 reveals that K1 featured a higher viscosity than K2, with the latter feedstock exhibiting relatively constant viscosity in the entire shear rate range of $0.1\text{--}100\ \text{s}^{-1}$. Conversely, at low shear rates, K1 exhibited high viscosity, which dramatically increased even further with increasing shear rate. Generally, feedstock viscosity is related to the flowability and packing ratio of constituent silica particles. Moreover, it is well known that the packing ratio of spherical particles is higher than that of angular ones [12]. Thus, at constant solid loading, temperature, binder, and shear rate, the mixture with the lowest viscosity should have the highest homogeneity [5]. In contrast to spherical particles, angular ones move in a certain preferred direction [6] when injected through small passages such as sprue, runner, gate, and cavity of the mold. Therefore, the homogeneity of feedstocks used for injection molding allows uniform mold filling and sintering, decreasing the extent of undesired separation or demixing [5]. Feedstock viscosity is a vital factor influencing the formation of injected green bodies. Fig. 4 shows a picture of two green bodies injection-molded using different feedstocks, demonstrating that the highly viscous one solidified before reaching the end of the mold and thus precluded the formation of a fully developed ceramic core. Additionally, shear rate is a function of both injected body thickness and injection

velocity, with the ratio of shear flow and thickness of a given structure fragment yielding the shear stress. The viscosity of K2 did not significantly change with shear rate. The blade and vane must keep its aerodynamic shape and hollow interior cooling passages by investment casting using ceramic shell and core. Thus, the ceramic core had a complicated shape, and its molds contained thin sections that were otherwise difficult to fill. As mentioned above, Fig. 4 provides examples of good and bad filling of injection molding feedstock, showing that feedstock K2 afforded a well-formed and defect-free injected green body and thus implying that this feedstock is not considerably influenced by the shear rate variation resulting from thickness variation.

The formation of cristobalite in the ceramic core after 12-h sintering at 1200°C was confirmed by XRD analysis (Figs. 5 and 6), with cristobalite and zircon phases detected in both cases. However, the two specimens showed slightly different cristobalite peak intensities. The cristobalite/zircon peak intensity ratio was calculated based on the ICDD database. The diffraction peak at $2\theta = 21.68^\circ$ was assigned to the cristobalite (110) plane according to JCPDS card No. 39-1425. Likewise, the strong diffraction peak at $2\theta = 26.86^\circ$ was assigned to the zircon (200) plane according to JCPDS card No. 6-266. Notably, K1 and K2 specimens contained the same zircon powders and featured identical formulations. All K2 specimens exhibited higher peak ratios (Table 2) than K1 ones, which indicated that crystallization in the former batch proceeded to a larger extent. The lower viscosity of K2

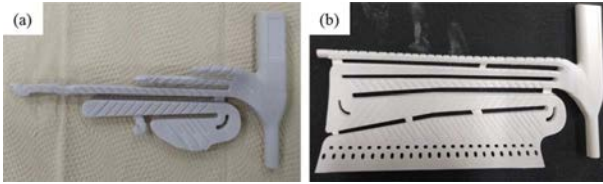


Fig. 4. Ceramic core formed by injection molding process at (a) high viscosity and (b) low viscosity.

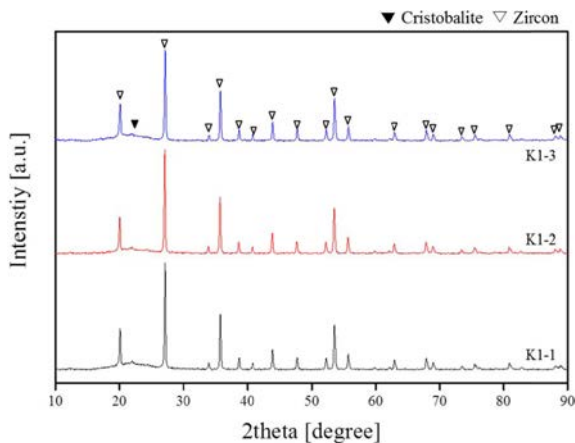


Fig. 5. X-ray diffraction patterns of K1 specimens.

Table 2. Peak ratio of K1 and K2 specimens sintered at 1200°C for 12 hours.

Sample (Angular)	Peak ratio	Sample (Spherical)	Peak ratio
K1-1	0.08	K2-1	0.10
K1-2	0.06	K2-2	0.12
K1-3	0.09	K2-3	0.11

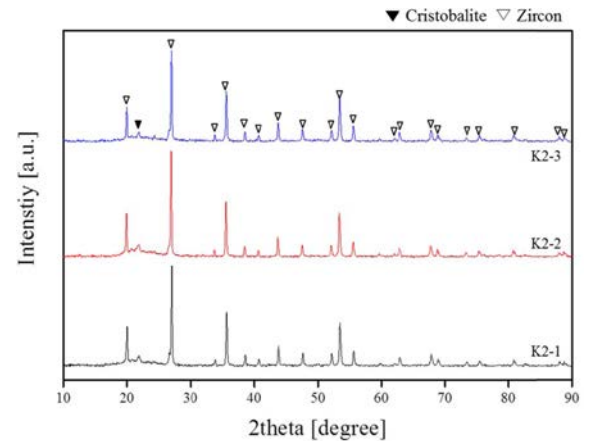


Fig. 6. X-ray diffraction patterns of K2 specimens.

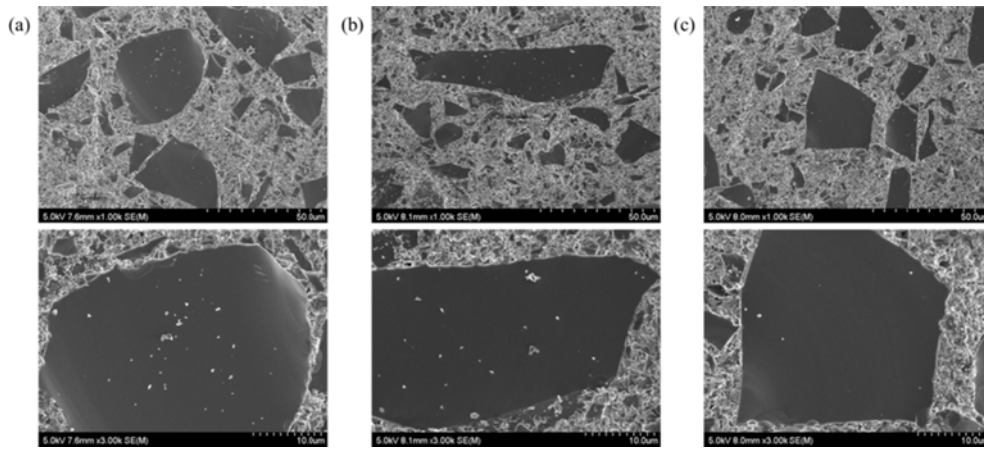


Fig. 7. Scanning electron microscope image of (a) K1-1, (b) K1-2 and (c) K1-3.

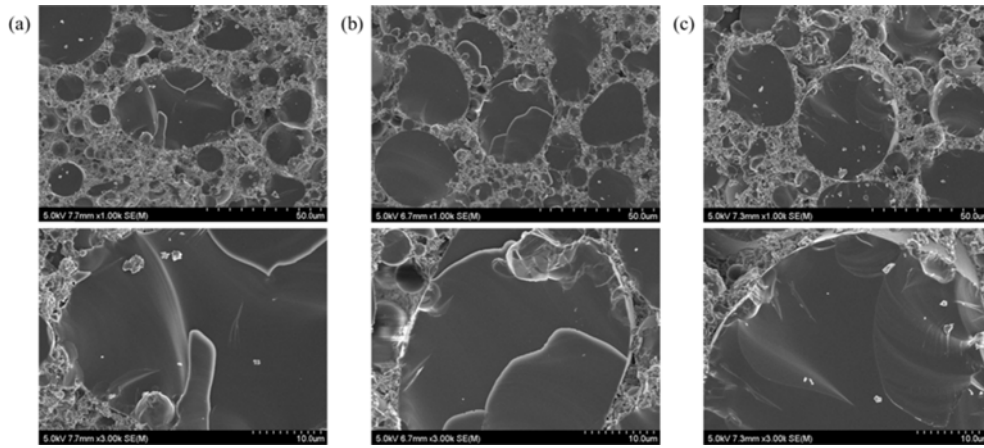


Fig. 8. Scanning electron microscope image of (a) K2-1, (b) K2-2 and (c) K2-3.

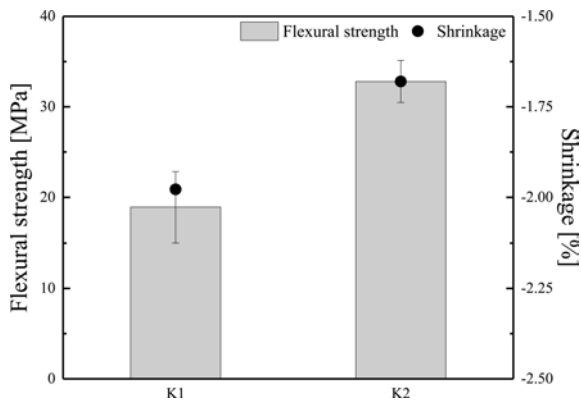


Fig. 9. Flexural strength and shrinkage of K1 and K2 specimens.

resulted in increased silica glass flowability, and the dense packing of spherical particles probably favored cristobalite crystallization on the surface of fused silica grains [13]. The XRD patterns in Fig. 6 also illustrated that K2 specimens had a higher degree of crystallinity than K1 ones, as reflected by the more pronounced cristobalite peaks observed in the former case. This result was in good agreement with that of SEM imaging. SEM images provided in Figs. 7 and 8 demonstrate that K2 specimens featured a larger

number of microcracks than K1 ones, i.e., transgranular fracture behavior was observed for smooth surfaces of spherical silica grains, whereas angular grains exhibited a small number of intergranular or transgranular fractures. Microcracking is commonly observed in the presence of cristobalite, and the crystallization of fused silica above 1380 °C is known to afford cristobalite deposited on the surface of fused silica particles [14, 15]. The present results were in good agreement with previous ones [4, 14, 16]. The β - to α -cristobalite transformation occurring at ~230 °C is accompanied by volume contraction, which results in microcracking. Thus, the abundance of microcracks was probably correlated with the relative content of cristobalite, with the usage of spherical silica particles thus facilitating the crystallization of fused silica.

To withstand wax patterning and shell molding processes, the ceramic core should be mechanically strong and dimensionally stable [1, 7, 17]. To probe the above properties, we measured the three-point flexural strength and linear shrinkage of K1 and K2 specimens after 12-h sintering at 1200 °C, revealing that the above samples exhibited strengths of 18.9 ± 3.9 and 32.8 ± 2.3 MPa, respectively, with the respective linear shrinkages equaling 1.98 and 1.68%. The obtained

values indicated that spherical particles had a beneficial effect on mechanical properties. As mentioned above, the presence of cristobalite was believed to decrease the strength of annealed samples due to inducing microcracking. However, this result contradicted the report of Niu [18], who investigated the effect of pre-added cristobalite content on the injection molding of feedstock containing fused silica and mullite. Increased contents of pre-added cristobalite decreased the flexural strength measured at room temperature and 1550 °C, additionally decreasing the shrinkage of the silica-based ceramic core. The cristobalite-rich K2 core showed enhanced strength and low shrinkage, which was attributed to low feedstock viscosity and the high packing ratio and surface area of constituent particles, i.e., the dense packing of spherical particles improved the mechanical properties of cores. The apparent porosities of K1 and K2 specimens were calculated based on Archimedes' principle, equaling 21.9 and 19.9%, respectively. Thus, the spherical silica batch showed lower porosity, i.e., a denser microstructure. The compact containing micro-sized spherical particles was more densified compared to the plate-like powder mixture [19]. Notably, the presence of cristobalite is a pre-requisite for silica-based formulations, being required for the development of high-temperature mechanical properties during the contact of ceramic cores with hot molten metal during investment casting. Thus, complex-shaped silica-zircon ceramic cores were successfully obtained using spherical silica powders.

Conclusions

Herein, we investigated the influence of particle morphology on the properties of ceramic cores by particle sizing, viscosity, flexural strength, linear shrinkage, porosity, SEM and XRD analyses. Despite spherical fused silica comprising finer particles with higher specific surfaces than angular silica, the former feedstock exhibited lower viscosity and excellent flow behavior. Moreover, the low viscosity of K2 resulted in an increased cristobalite content of these specimens, as confirmed by XRD and SEM analyses. Nevertheless, K2 specimens had a higher flexural strength and lower linear shrinkage than K1 ones due to having a denser particle packing, consequently exhibiting improved mechanical strength and an increased rate of cristobalite crystallization.

Acknowledgments

This work was supported by the Power Generation and Electricity Delivery Core Technology Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP), granted financial resource from the Ministry of Trade, Industry and Energy, Republic of Korea (20141020102460).

References

1. C. Huseby, M.P. Borom, C.D. Greskovich, *Am. Ceram. Soc. Bull.* 58 (1979) 448-452.
2. W.D. Kingery, H.K. Bowen, D.R. Uhlmann, in "Introduction to Ceramics", John Wiley & Sons, U.S.A., (1960) 589-595.
3. L.Y. Wang, M.H. Hon, *J. Ceram. Soc. Jpn.* 102[6] (1994) 517-521.
4. J.G. Yeo, Y.H. Kim, J.S. Park, S.C. Choi, *J. Ceram. Proc. Res.* 17, (2016) 885-889.
5. R.M. German, *J. Am. Ceram. Soc.* 77[1] (1994) 283-285.
6. A. Mannschatz, A. Müller, T. Moritz, *J. Eur. Ceram. Soc.* 31 (2011) 2552-2558.
7. Y.H. Kim, J.G. Yeo, S.C. Choi, *J. Kor. Ceram. Soc.* 53[2] (2016) 246-252.
8. J.J. Liang, Q.H. Lin, X. Zhang, T. Jin, Y.Z. Zhou, X.F. Sun, B.G. Choi, I.S. Kim, J.H. Do, C.Y. Jo, *J. Mater. Sci. Technol.* 33[2] (2017) 204-209.
9. N. Kivi, A. Moore, K. Dyar, S. Haaf, University of Tennessee Honors Thesis Projects (2016).
10. ASTM C1161-13, ASTM International, West Conshohocken, PA, U.S.A., (2013).
11. R. Cepuritis, E. J. Garboczi, C. F. Ferraris, S. Jacobsen, B. E. Sørensen, *Adv. Powder Tech.* 28 (2017) 706-720.
12. B.C. Mutsuddy, R.G. Ford, in "Ceramic injection molding", Chapman & Hall, U.K., (1995) 27-30.
13. A. Kazemi, M.A. Faghihi-Sani, H.R. Alizadeh, *J. Eur. Ceram. Soc.* 33 (2013) 3397-3402.
14. R.C. Breneman, J.W. Halloran, *J. Am. Ceram. Soc.* 98[5] (2015) 1611-1617.
15. A. Kazemi, M.A. Faghihi-Sani, M.J. Nayyeri, M. Mohammadi, M. Hajfathalian, *Ceram. Int.* 40 (2014) 1093-1098.
16. Y.H. Kim, J.G. Yeo, J.S. Lee, S.C. Choi, *Ceram. Int.* 42 (2016) 14738-14742.
17. G.H. Cho, E.H. Kim, Y.G. Jung, *J. Kor. Ceram. Soc.* 53[5] (2016) 541-547.
18. S.X. Niu, D.Z. Tang, X.G. Liu, J.S. Yao, X. Li, L. Wang, G. Gu, Y. Yang, X. Yang, *Mater. Sci. Forum.* 80 (2016) 217-221.
19. S. Taruta, K. Kitajima, B. Takusagawa, Y. Takagai, K. Okada, N. Otsuka, *J. Mat. Sci. Lett.* 12 (1993) 424-426.