

용융탄산염 연료전지를 위한 나노 알루미늄을 이용한 강화 매트릭스의 기계적 강도 증진

김형석^{1,2} · 송신애¹ · 장성철^{1,3} · 박동녕¹ · 함형철¹ · 윤성필¹ · 오성근³ · 한중희^{1†} · 김성현^{2†}

¹한국과학기술연구원(KIST) 연료전지연구센터, ²고려대학교 그린스쿨대학원 에너지환경정책기술학과, ³한양대학교 화학공학과

Enhancement of Mechanical Strength Using Nano Aluminum Reinforced Matrix for Molten Carbonate Fuel Cell

HYUNGSUK KIM^{1,2}, SHINAE SONG¹, SEONGCHEOL JANG^{1,3}, DONGNYEOCK PARK¹,
HYUNGCHUL HAM¹, SUNGPIL YOON¹, SEONGGEUN OH³, JONGHEE HAN^{1†}, SUNGHYUN KIM^{2†}

¹Fuel Cell Research Center, Korea Institute of Science and Technology, Hwarangno 14-gil 5,
Seongbuk-gu, Seoul, 136-791, Republic of Korea

²Department of Energy Environmental Policy Technology, Green School, Graduate school of Energy and Environment,
Korea University, 145 Anam-ro, Seongbuk-gu, Seoul, 136-701, Korea

³Major in Chemical Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-gu,
Seoul, 133-791, Republic of Korea

Abstract >> 용융탄산염 연료전지 상용화를 위해서 40,000 시간이상 장기 운전이 가능해야 한다. 장기운전을 위해 크랙 발생이 적고 기계적 강도가 높은 강화 매트릭스의 개발이 절실히 요구되고 있다. 본 연구에서는 LiAlO₂에 알루미늄 나노입자를 첨가하여 매트릭스의 기계적 강도를 향상시키는 연구를 수행하였다. 나노 알루미늄 첨가 LiAlO₂ 그린 시트를 수소 분위기에서 열처리한 결과, 공기 분위기에서 열처리한 매트릭스에 비해 기계적 강도가 1.5배 증가함을 확인하였다. 이는 환원분위기에서 열처리를 할 경우, 알루미늄의 입자간의 소결으로 인한 neck이 형성 되어 LiAlO₂ 입자 간에 다리를 만들어주는 효과가 나타나 매트릭스의 기계적 강도가 크게 증진되었으리라 판단된다.

Key words : MCFC(용융탄산염전지), Reinforced matrix(강화매트릭스), Sintering(소성), Aluminium(알루미늄), Reducing atmosphere(환원성 분위기)

1. Introduction

The molten carbonate fuel cell (MCFC) has been regarded as a promising alternative energy source for power generation systems because its electrochemical

conversion efficiency is high, it offers fuel flexibility, it is environment friendly, and it provides combined heat and power (CHP)¹⁻³. Nowadays, MCFC prepares to enter the stage of commercialization. For commercialization, a 40,000h operation time of the MCSC stacks should be guaranteed. One of the most important factors for long-term operation is ensuring the stability of the matrix that plays an important role both as a reservoir of liquid electrolyte and as an

[†] Corresponding author : jhan@kist.re.kr
Kimsh@korea.ac.kr

[접수일 : 2012.3.28 수정일 : 2012.4.23 게재확정일 : 2012.4.27]

inhibitor between the cathode and anode. Further, cracks that are formed in the matrix during cell operation dramatically deteriorate the cell performance due to the direct reaction between H_2 and O_2 (not the electrochemical reaction)^{4,5}; this deterioration in the cell performance also prevents long-term operation of MCFC stacks for over 40,000h. To prevent crack formation during cell operation, increasing the mechanical strength of the matrix is important. Several studies have been conducted and several approaches have been considered to increase the mechanical strength of the matrix.

Two types of approaches are employed to increase the mechanical strength of the matrix: one approach involves the addition of sintering aids such as boron oxide (B_2O_3) and aluminum acetylacetonate ($(C_5H_7O_2)_3Al$) for reinforcing the $LiAlO_2$ matrix and the other involves the addition of crack attenuators such as rod-shaped γ - $LiAlO_2$ and Al powders ($3\ \mu m$ and $30\ \mu m$)⁶⁻¹¹. In the first approach, neck formation between $LiAlO_2$ particles occurs due to the low melting or vaporization temperatures of sintering aids, which are less than $650\ ^\circ C$, the operating temperature of MCFC. Below $650\ ^\circ C$, the molten boron oxide causes liquid-phase sintering of the $LiAlO_2$ matrix or the aluminum acetylacetonate vapor acts as the adhesive causing the sintering of the matrix. It is reported that the neck formation between $LiAlO_2$ particles because of sintering aids increase the mechanical strength dramatically. However, thus far, results of tests on single cells with the reinforced matrices and sintering aids have not been conclusive^{7,8}.

When crack attenuators are to be used, either particles with different shapes such as rod-shaped γ - $LiAlO_2$ ⁹ or large particles such as $3\ \mu m$ or $30\ \mu m$ aluminum particles^{10,11} can be added. In both cases, the particles with different shapes and sizes are

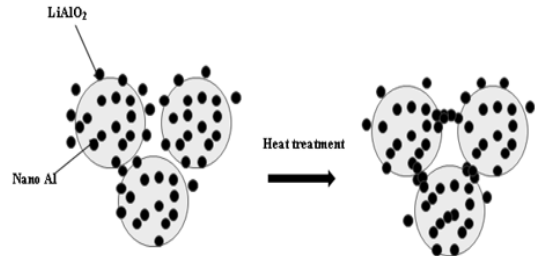


Fig. 1 Schematic illustration illustrating reactive sintering of nano aluminum particles and $LiAlO_2$

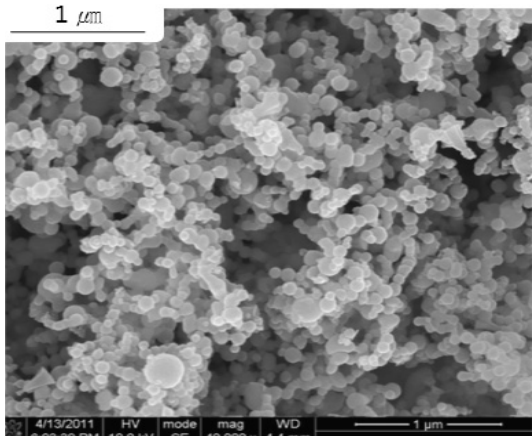
expected to act as inhibitors against the progression of the cracks formed during the cell operation. Currently, these methods are widely used for increasing the mechanical strength of the matrix. However, the requirements for the commercialization of MCFC systems are still not satisfied¹².

In this study, we propose a new concept for the reinforcement of the $LiAlO_2$ matrix. This new concept is the improvement of the mechanical strength by bridge formation between $LiAlO_2$ particles, using nano Al particles, as shown in Fig. 1. Since the melting point of Al is low (around $660\ ^\circ C$), neck formation between Al particles is expected during the pretreatment process. It is also expected that sintering Al particles improves the mechanical strength of the matrix, and thus, long-term operation becomes possible.

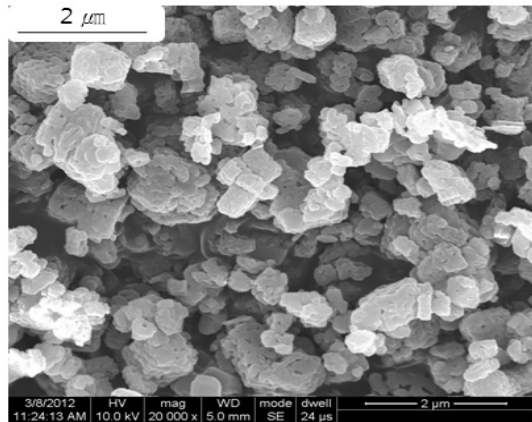
In order to confirm whether this concept of reinforced matrix is feasible, matrices containing nano Al were fabricated by the conventional tape casting method. The prepared matrices containing the nano Al were heated in a H_2 atmosphere and in air, and then, their mechanical strengths were examined and compared by performing a three-point bending strength test.

2. Experimental

In order to fabricate a matrix green sheet reinforced with nano Al, a commercial α - $LiAlO_2$



(a)



(b)

Fig. 2 SEM images of pure (a) nano Al powder and (b) α -LiAlO₂ powders

powder (Chemetall Foote Co.; average particle size: 2 μ m) and nanosized Al powder (Nano Technology Chemical Co.; average particle size: 100 nm) were used. Fig. 2 shows the SEM images of the pure α -LiAlO₂ and nano Al powders used for reinforcing the matrix.

As shown in Fig. 2, α -LiAlO₂ particles have irregular shapes and a size of about 2 μ m and Al particles have a spherical shape and a size of about 100 nm.

Fig. 3 shows the procedure for the fabrication of reinforced matrix green sheet by employing tape casting method. A mixture of raw commercial α

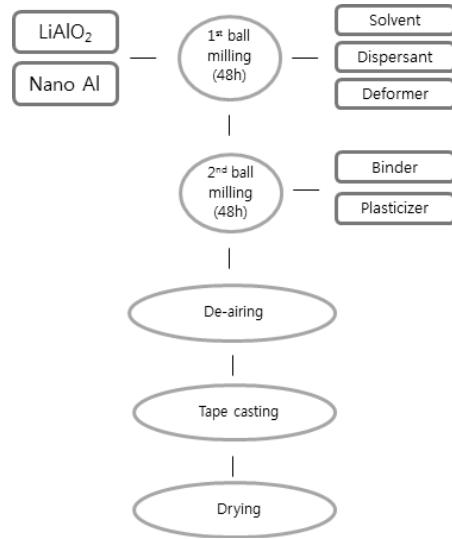


Fig. 3 Flowchart of the fabrication process of matrix reinforced with nano aluminum

-LiAlO₂ powder, Al powder, Li₂CO₃ (Junsei chemical Co.), a dispersant (DisperBYK-110, BYK Chemie Co.), a defoamer (SND 348, San Nopco, Korea) and an organic solvent [a 7:3 (w/w) mixture of toluene (99.5%, Deajung Co.) and anhydrous ethyl alcohol (99.0%, Deajung Co.)] was ball-milled for 48h. Then, a binder (polyvinyl butyral, Solutia Co.) and a plasticizer (dibutyl phthalate, Junsei chemical Co.) were added into the slurry and this mixture was again ball-milled for 48h. This prepared slurry was de-aired under vacuum and tape-casted using a doctor blade and the resultant tapes were dried at 100 °C. Finally, the nano Al added α -LiAlO₂ matrix with 0.3 mm thickness was obtained. The amount of added nano Al powder was fixed at 20wt.% of total powder mixture.

To prevent the oxidation of Al and to induce sintering of Al particles, the prepared matrix was heat-treated in a H₂ atmosphere at several temperatures (400, 450, 500 °C). Heat-treatment in air was also performed, and the heat-treated matrices were compared. To measure the mechanical strength, matrix samples

with identical size of 10 mm × 5 mm × 0.3 mm were prepared.

To evaluate the mechanical strengths of the matrix samples, a three-point bending strength test was carried out at room temperature using bending test machine (QC-508E, Cometech Co.). This test is one of the most commonly used methods for measuring the mechanical strength of the matrix^{13,14}. The compressive force (50 N) applied directly to the sample surface was controlled by QCTechB software. After three time measurements, the ratios of the loading stress to sample displacement were obtained.

The three-point bending strength can be calculated by using the following equation.

$$\sigma = \frac{3PL}{2bd^2} \quad (1)$$

where, σ (g/mm^2) is the three-point bending strength, P (N) the fracture load; L (mm) the span distance; b (mm) the specimen width; and d (mm) the specimen thickness.

The crystal structure or the microstructure of nano Al reinforced matrix were examined using X-ray diffraction (XRD, Rigaku, Co.) and scanning electronic microscopy (SEM, NOVA NanoSEM200).

3. Results and Discussion

Fig. 4 shows the mechanical strengths of the matrices that were with and without 20 wt.% nano Al and that were heat-treated in H_2 atmosphere and air. The mechanical strength of the matrix with nano Al increased, regardless of same heat-treatment atmosphere. In general, it is well known that the addition of nanoparticles into a ceramic membrane improves the mechanical strength of matrix because of the large

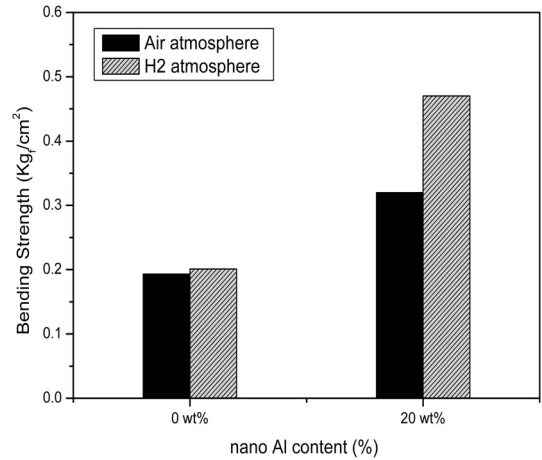
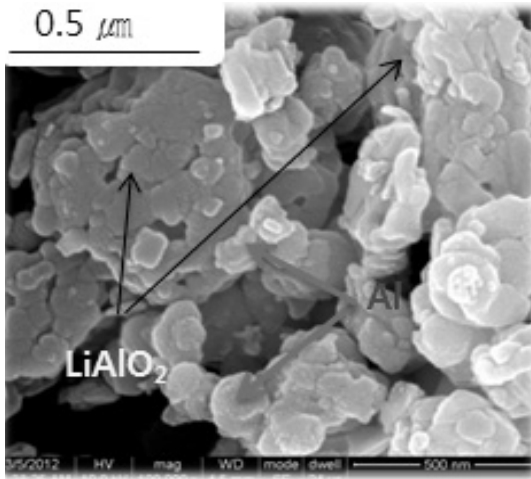


Fig. 4 Mechanical strengths of the non-reinforced matrix and nano-Al-reinforced matrix after heat-treatment in air and H_2 atmosphere

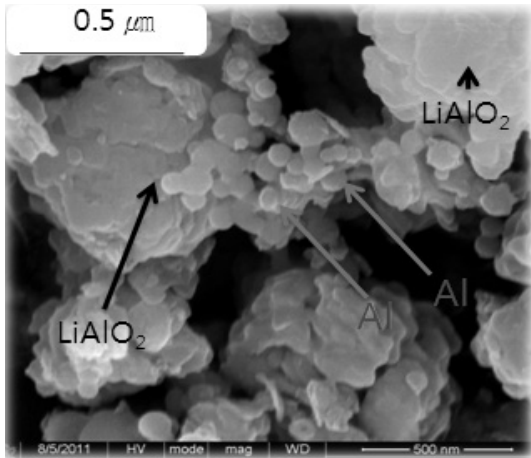
surface-to-volume ratio of nanoparticles¹⁵).

As shown in Fig. 4, the mechanical strength of the reinforced matrix heat-treated in the H_2 atmosphere is 1.5 times larger than that the matrix heat-treated in air. This interesting result shows indirectly that a different mechanism for enhancing mechanical strength not the effect of addition of nanoparticles works on the nano Al reinforced matrix heat-treated in H_2 atmosphere.

To understand why the mechanical strength of reinforced matrix heat-treated in the reducing atmosphere is significantly increased, the microstructures of the reinforced matrices heat-treated in air and in the H_2 atmosphere were examined and compared by performing SEM analysis (Fig. 5). As shown in the SEM images, in the case of the reinforced matrix heat-treated in a reducing atmosphere, bridges between LiAlO_2 particles, formed by neck formation between nano Al particles are observed, while no bridge can be found in the sample heat-treated in air. It appears that the bridge formation observed in the sample heat-treated in the reducing atmosphere increases the mechanical strength of the reinforced



(a)



(b)

Fig. 5 SEM images of matrices reinforced with nano Al (a) after heat-treatment at 450°C in air for 200h and (b) after heat-treatment at 450°C in H₂ atmosphere for 200h

matrix to a greater extent than the addition of nanoparticles does.

In case of the sample heat-treated in air, nano Al particles in the matrix oxidize to Al₂O₃. Unfortunately, Al₂O₃ cannot form the bridge between LiAlO₂ particles by sintering between Al particles due to the high melting point of Al₂O₃ (around 2075°C)

However, in the case of the sample heat-treated in the H₂ atmosphere, the bridge formation between

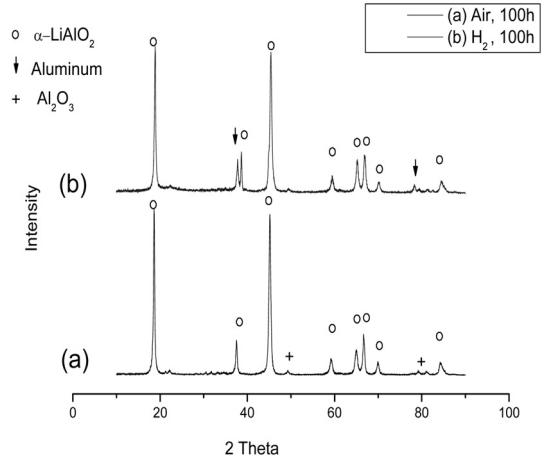


Fig. 6 XRD patterns of matrix reinforced with nano Al (a) after heat-treatment at 450°C in air for 100h and (b) after heat-treatment at 450°C in H₂ atmosphere for 100h

LiAlO₂ particles by neck formation among nano Al particles is possible, because of the low melting point of Al (around 660 °C). By using XRD data, we can confirm the difference between Al states in matrices heat-treated in air and the H₂ atmosphere. Fig. 6 shows the XRD patterns of the two samples heat-treated in air and the H₂ atmosphere at 450 °C for 100 h. As shown in this figure, Al peaks near 2θ values of 38.47° and 78.23° are observed in the case of the sample heat-treated in the H₂ atmosphere, whereas only Al₂O₃ (not Al) was found in the sample heat-treated in air. As mentioned above, heat-treatment in air oxidizes Al in the matrix to Al₂O₃ and the neck formation between Al particles will be impossible. In this case, only the addition of nanoparticles contributes to the reinforcement of the matrix. However, in the case of samples heat-treated in the reducing atmosphere, Al remains unchanged with low melting temperature. Thus, Al can be sintered neck formation occurs, which significantly improves the mechanical strength of the reinforced matrix.

To investigate the effect of the heat-treatment temperature on the mechanical strength of nano-Al-

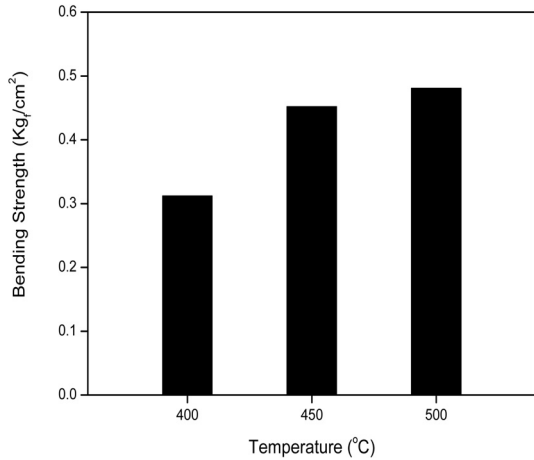


Fig. 7 Mechanical strengths of nano Al reinforced matrix with increasing heat-treatment temperatures

reinforced matrix, the mechanical strengths of matrices heat-treated at various temperatures are measured, as shown in Fig. 7. The nano Al content in the matrix was fixed at 20 wt%. As shown in Fig. 7, the mechanical strength of nano Al-reinforced matrix increases considerably at 450 °C, and beyond 450 °C, it increases slowly.

It is well known that sintering of two particles starts at a temperature that is two-thirds of the particle melting point¹⁶⁾. Since the melting point of Al is 660 °C, the neck formation by sintering of Al particles is expected to start at around 450 °C. Thus, it is thought that the mechanical strength is increased at 450 °C. The fact that the bending strength values of samples heat-treated in air and of those heat-treated in the H₂ atmosphere at 400 °C are similar shows that the reinforced mechanism of nano Al reinforced matrix change to bridge effect by sintering between Al particles from simple effect by the addition of nano particles.

4. Conclusions

The LiAlO₂ matrix reinforced by the addition of

nano Al has been prepared successfully. The mechanical strength of the reinforced matrix heat-treated in a H₂ atmosphere is 1.5 times greater than that of the reinforced matrix heated in air, because of a difference in the reinforcement mechanism. In the sample heat-treated in the reducing atmosphere, nano Al particles in the matrix form bridges between LiAlO₂ particles as a result of sintering of the nano Al particles due to the low melting point of Al (near 660 °C), thus increasing the mechanical strength of the matrix. In the sample heat-treated in air, only the addition of nanoparticles affects the mechanical strength of the matrix. The reinforced matrix described in this study is expected to improve the long-term stability of MCFC cell.

Acknowledgement

This work was supported by the Renewable Energy R&D Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Ministry of Knowledge Economy, Republic of Korea (No. 2011T100200055).

Reference

1. L. Zhou, H. Lin, and B. Yi, "Sintering behavior of porous α -lithium aluminate matrices in molten carbonate fuel cells at high temperature", *J. Power Sources*, Vol. 164, 2007, pp. 24-32.
2. S. A. Song, J. Han, S. P. Yoon, S. W. Nam, I. H. Oh, and D. K. Choi, "Economic feasibility study for molten carbonate fuel cells fed with biogas", *J. Electrochem. Sci. Tech.*, Vol. 1, 2010, p. 102.
3. D. Marra, and B. Bosio, "Process analysis of 1MW MCFC plant", *Int. J. Hydrog Energy* Vol. 32, 2007, p. 809.
4. Y. Y. Kim, J. H. Han, and T. H. Lim, "The

- effect of the matrix thickness on the long term performance of MCFC”, *Trans. of Korean Hydrogen and New Energy Society*, Vol. 16, 2005, pp. 170-179.
5. K. Tanimoto, M. Yanagida, “Long-term operation of small-sized single molten carbonate fuel cells”, *J. Power Sources*, Vol. 72, 1998, pp. 77-82.
 6. H. J. Chio, M. Y. Shin, S. H. Hyun, H. C. Lim, “Optimization of Rod-shaped γ -LiAlO₂ Particle Reinforced MCFC Matrices by Aqueous Tape Casting”, *J. Korean Ceram. Soc.*, Vol. 46, 2009, pp. 282-287.
 7. H. C. Hahm, S. P. Yoon, J. Han, S. W. Nam, T.H. Lim, and S.-A. Hong, “Development of reinforced matrix for molten carbonate fuel cells by using sintering aids”, *ECS Transactions*, Vol. 5, No.1, 2007, p. 445.
 8. I. S. Lee, W. S. Kim, D. Y. Lee, “Influence of aluminum salt addition on in situ sintering of electrolyte matrices for molten carbonate fuel cells”, *J. of power sources*, Vol. 34, 2001, pp. 90-95.
 9. H. S. Hyun, C. S. Cho, “Reinforcement of molten carbonate fuel cell matrixes by adding rod-shaped gamma-LiAlO₂ particles”, *J. Mater. Sci.*, Vol. 36, 2001, p. 441.
 10. J.-J. Lee, H. J. Choi, S. H. Hyun, and H. C. Lim, “Characteristics of aluminum-reinforced LiAlO₂ matrices for molten carbonate fuel cells”, *J. Power Sources*, Vol. 179, 2008, p. 504.
 11. J. E. Kim, K. Y. Patil, J. Han, S. P. Yoon, S. W. Nam, T. H. Lim, “Using aluminum and Li₂CO₃ particles to reinforce the α -LiAlO₂ matrix for molten carbonate fuel cells”, *Int. J. Hydrogen Energy*, Vol. 34, 2009, p. 9227.
 12. H.-J. Choi, J.-J. Lee, S.-H. Hyun, and H.-C. Lim, “Phase and microstructural stability of electrolyte matrix materials for molten carbonate fuel cells”, *Fuel cells*, Vol. 10, 2010, p. 613.
 13. J. -J. Lee, H. -J. Choi, S. -H. Hyun, H. -C. Im, “CHaracteristics of aluminum-reinforced γ -LiAlO₂ matrices for molten carbonate fuel cells”, *J. Powder Sources*, Vol. 179, 2008, p. 504.
 14. S. H. Hyun, S. C. Cho, J. Y. Cho, D. H. Ko, *J. Mater. Sci.*, Vol. 36, 2001, p. 441.
 15. M. R. Noordin, and K. Yong Liew (2010), “synthesis of alumina nanofibers and composites”, *Nanofibers*, A. Kumar (Ed.), ISBN: 978-953-7619-86-2, InTech, Available from: <http://www.intechopen.com/books/nanofibers/synthesis-of-alumina-nanofibers-and-composites>
 16. U. Schubert, N. Husing, “Synthesis of inorganis materials”, Third edtion, Wiley-VCH Verlag & CO. KGaA, Germany, 2012, p. 35.