HOSTED BY

Contents lists available at ScienceDirect

Journal of Asian Ceramic Societies

journal homepage: www.elsevier.com/locate/jascer

ELSEVIER

JAsCerS

2014

Seeding technique for lowering temperature during synthesis of α-alumina

CrossMark

Yoshio Kobayashi [a,*], Yusuke Mabuchi [a], Masachika Hama [a], Kazuhiro Inoue [a], Yusuke Yasuda [b], Toshiaki Morita [b]

[a] Department of Biomolecular Functional Engineering, College of Engineering, Ibaraki University, 4-12-1 Naka-narusawa-cho, Hitachi, Ibaraki 316-8511, Japan
[b] Hitachi Research Laboratory, Hitachi Ltd., 7-1-1 Omika-cho, Hitachi, Ibaraki 319-1292, Japan

ARTICLE INFO

ABSTRACT

This paper reports a method for producing α-Al_2O_3 at low temperature using a seeding technique. A white product obtained by hydrolyzing aluminum isopropoxide in water at 80 °C was peptized using acetic acid at 80 °C, which transformed the white product to a transparent alumina sol. α-Al_2O_3 particles were added to the alumina sol as seed material; the sol containing α-Al_2O_3 particles was then transformed to an α-Al_2O_3-seeded alumina gel by drying the sol at room temperature. The non-seeded alumina gel remained boehmite after annealing at 300 °C and crystallized into γ-Al_2O_3 and α-Al_2O_3 at temperatures between 300 and 500 °C and between 900 and 1100 °C, respectively. The α-Al_2O_3 seeding promoted crystallization of the alumina gel into α-Al_2O_3. The promotion of crystallization was significant with an increase in α-Al_2O_3 particle content by weight in the final seeded alumina gel. With an α-Al_2O_3 particle content of 5%, the seeded alumina gel was partially crystallized into α-Al_2O_3 by annealing at a temperature as low as 900 °C.

1. Introduction

Electrically conductive materials, such as gold, silver and copper, and electrically insulating materials are essential for producing electronic devices such as integrated circuits. Alumina is a representative electrically insulating material that has high thermal conductivity and high chemical stability at high temperatures compared to other electrically insulating materials, such as glass, plastic and paper [1–5]. Its characteristics make it applicable for use as an electrically insulating material in electronic devices.

There are various crystal structures in alumina; among them is the electrically insulative α-type. α-Alumina has been conventionally produced by annealing aluminum hydroxide derived from aluminum salts or minerals at temperatures higher than 1000 °C [6–8]. This method requires high temperatures and thus a high amount of energy. As a result, low temperature processes for producing α-alumina are desired for saving energy.

This study has described the effects of nanocrystallite seeding on various titanates, such as PZT and BST, fabricated using the sol–gel method, which has been used in this area of research for the last decade [9–12]. As a result, the materials' crystallization temperatures were lowered with seeding; the surface of the crystallites promoted the crystallization of titanates as a starting point for crystallization, lowering the crystallization temperatures. Accordingly, the crystallization temperature of alumina (i.e., the temperature for transformation of amorphous alumina to α-alumina) is likely to be lowered with the seeding technique.

The author's previous work proposed methods for preparing alumina sol from inorganic aluminum salt using a homogeneous precipitation method and for fabricating alumina [13]. The obtained alumina consisted of amorphous or fine crystallites even after annealing at temperatures as high as 500 °C and was crystallized to γ-Al_2O_3 at 900 °C, which implied that the alumina must be annealed at even higher temperatures to produce transformations to α-Al_2O_3. According to another previous work [14], the alumina produced by the homogeneous precipitation method was partially crystallized to α-Al_2O_3 by annealing at a temperature as low as 700 °C but primarily at 900 °C by seeding of α-Al_2O_3 nanocrystallites. Because inorganic aluminum salt was used as a starting chemical, anions derived from the salt would remain in the alumina.

* Corresponding author. Tel.: +81 294 38 5052; fax: +81 294 38 5078.
E-mail address: ykoba@mx.ibaraki.ac.jp (Y. Kobayashi).

The existence of these ions may spoil the electrically insulating properties of the alumina.

Alumina can also be fabricated by a sol–gel process using aluminum alkoxide as a starting chemical [15–17]. The obtained alumina contains fewer inorganic ions compared to that produced from inorganic aluminum salt. Although a large amount of alcohol derived from the aluminum alkoxide would remain in the alumina, the alcohol can be removed by annealing at high temperatures.

The aim of the present work is to study the effect of α-alumina seeding on the crystallization of alumina fabricated from aluminum alkoxide and to lower the annealing temperature for the production of α-Al$_2$O$_3$.

2. Materials and methods

2.1. Materials

Aluminum isopropoxide (98.0%) was used as a starting material for alumina. Acetic acid (99.7%) was used as a peptizer for the aluminum compound produced by hydrolysis of aluminum isopropoxide. The seed crystallite used was α-Al$_2$O$_3$ (99.85%, Ionic Liquids Technologies); according to its manufacturer's data, this material has a particle size of 150 nm. Except for the aluminum isopropoxide and the α-Al$_2$O$_3$ seed crystallite, all chemicals were purchased from Kanto Chemical Co., Inc. and were used as received. Water that was ion-exchanged and distilled with a Yamato WG-250 was used in all preparations.

2.2. Preparation

Alumina sol was prepared by hydrolyzing the aluminum isopropoxide and by then peptizing the aluminum compound obtained via hydrolysis; the following procedure may have also been used. The aluminum isopropoxide was vigorously stirred in water at 80 °C for 1 h. Acetic acid was then added to the slurry, and the stirring was continued for the next 8 h for peptization. The initial concentration of aluminum isopropoxide and acetic acid were 0.56 and 0.084 M, respectively. The α-Al$_2$O$_3$ seed crystallites were dispersed in the mixture at 1–10% by weight for the final alumina. Then, the mixture containing the particles was cast onto a petri dish. Drying in air at room temperature converted the mixture into a solid film. The alumina sol was dried at room temperature, until the sol was converted to a solid film and the film was spontaneously peeled off from the petri dish in a few days. The peeling-off was regarded as the completion of drying in the present work. The film was pulverized with a mortar into powder and then annealed in air at various temperatures with a Yamato FO100 muffle furnace. The heating rate until the temperature in furnace reached the target annealing temperature was set as 10 °C/min. The annealing time was 2 h, which was determined by following our previous works on alumina that have been performed in these ten years [18].

2.3. Characterization

The sols were characterized by ultra-visible (UV–vis) spectroscopy, dynamic light scattering (DLS) and electrophoretic light scattering (ELS). UV–vis extinction of the sol was measured with a Shimadzu UV-3101PC (Kyoto, Japan) spectrophotometer. The size distribution and ζ-potentials of the particles in the sols were measured using DLS and ELS, respectively, to obtain information about the state of the particles. Both DLS and ELS were performed using a Brookhaven Zeta-Plus instrument (Holtsville, New York, USA). An aqueous solution of HCl or NaOH was added to the sample to alter the pH for the ELS measurements. The morphology of the α-Al$_2$O$_3$ seed crystallite was characterized by transmittance electron microscopy (TEM), which was performed with a JEOL JEM-2000FX
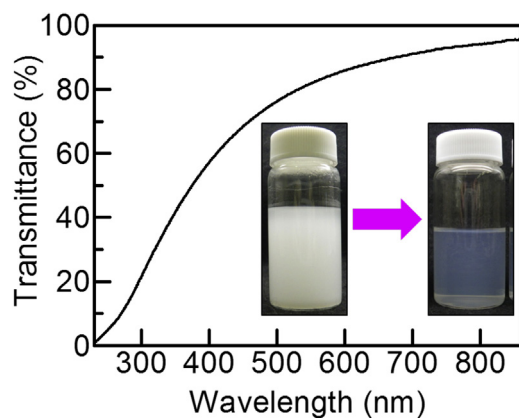

Fig. 1. UV–vis transmittance spectrum of alumina sol. Left and right insets show photographs of aluminum isopropoxide in water prior to and after peptization, respectively.

II (Akishima, Tokyo, Japan) operating at 200 kV. TEM samples were prepared by dropping and evaporating the alumina sol onto a collodion-coated copper grid. The gels were characterized by X-ray diffractometry (XRD). Powder that was obtained by pulverizing the alumina gel film with a mortar was used as samples for XRD measurements. The XRD measurements were performed with a Rigaku Ultima IV X-ray diffractometer at 40 kV and 30 mA with CuKα$_1$ radiation.

3. Results and discussion

3.1. Alumina sol

The insets of Fig. 1 show photographs of the mixture of aluminum isopropoxide and water prior to and after peptization. Prior to peptization, the mixture could be described as a white slurry, in which the aluminum compound produced by hydrolysis of the aluminum isopropoxide was well suspended in water. The suspension became a transparent sol after peptization, though it was slightly opaque; the sol was then called an alumina sol. Fig. 1 shows a UV–vis transmittance spectrum of the alumina sol. Transmittance was over ca. 80% in a range of wavelengths above 500 nm.

The inset of Fig. 2 shows a TEM image of particles in the alumina sol. Quasi-spherical particles were observed with an average size of 8.8 ± 2.6 nm. Fig. 2 shows their size distribution, as obtained by
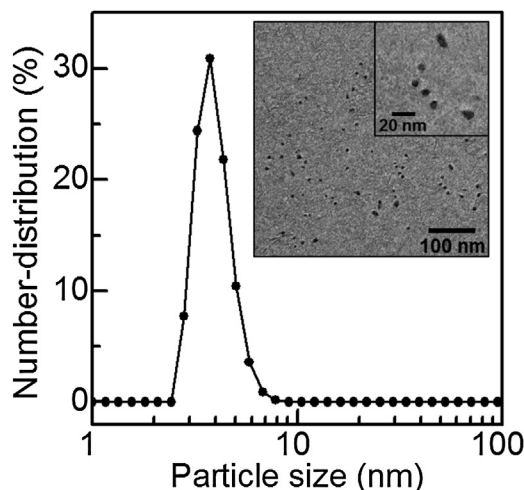

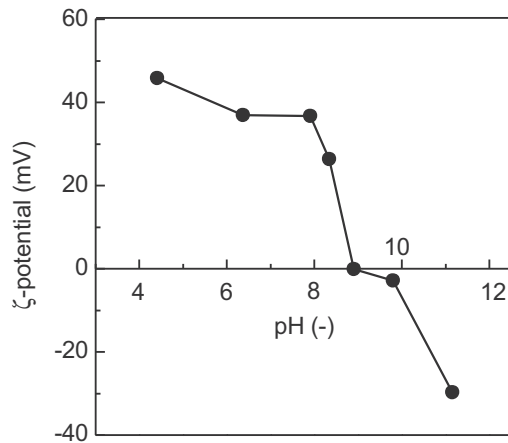**Fig. 2.** Size distribution of particles in alumina sol measured by DLS. Inset shows TEM image of the particles.

Fig. 3. ζ-Potential of particles in alumina sol measured by ELS vs. pH.

DLS. The particles were monodispersed, and the particle size was distributed near 3.8 nm. This size roughly corresponded to the size estimated by TEM observation.

Fig. 3 shows a ζ-potential of the particles in sol as a function of its pH. With increasing pH, ζ-potential with positive values decreased, passed through the isoelectric points into negative values and then decreased further. An isoelectric point (IEP) of the particles was 8.9, which indicates that the particles were cationic in a neutral pH range. There are various kinds of aluminas in crystal structure. According to several works on alumina [19–23], their IEPs are in a range as narrow as 8.6–9.8. The IEP of 8.9 was obtained in the range as in the present work, which implied that the particles in sol had surface similar to that of alumina.

3.2. Alumina gel films

The alumina sol became a solid film by gelation after drying on the petri dish. The film was called an alumina gel film at this stage. Fig. 4 shows photographs of the aluminum gel films annealed at various temperatures. The as-prepared films were transparent but then gradually became opaque with an increase in annealing temperature. For the film annealed at 900 °C, which was still transparent, it was easy to see the letters "alumina" through the film. In contrast, this was difficult with the film annealed at 100 °C due to a loss of clarity. This drastic change in transmittance implied that the film was transformed to α-Al$_2$O$_3$ at a temperature between 900 and 1100 °C because α-Al$_2$O$_3$ is a white solid.

Fig. 5 shows the XRD patterns of the alumina gel films annealed at various temperatures. Several peaks were detected near 14.4°, 28.0°, 38.8°, 49.0°, 64.9° and 72.3° in the as-prepared alumina gel film and in the films annealed at 100 and 300 °C. These peaks were assigned to those of boehmite, according to reference [24] and a JCPDS card (#21-1307). For the gel annealed at 500 °C, peaks were detected near 31.9°, 37.3°, 39.5°, 45.5° and 66.7°. According to reference [24] and a JCPDS card (#29-0063), these peaks can be attributed to γ-Al$_2$O$_3$, which indicated that transformation from boehmite to γ-Al$_2$O$_3$ had occurred at a temperature between 300 and 500 °C. There was no large difference in the XRD pattern of γ-Al$_2$O$_3$ among the annealing temperatures of 500, 700 and 900 °C. Sharp peaks appeared at 25.6°, 35.2°, 37.9°, 43.5°, 52.6°, 57.5°, 61.4°, 66.6° and 77.0°, with an increase to 1100 °C, which could be attributed to α-Al$_2$O$_3$, according to reference [25] and a JCPDS card (#42-1468); these sources indicated that the 1100 °C annealing promoted the crystallization of alumina gel to α-Al$_2$O$_3$ and supported the implications obtained from the photographs of alumina gel films shown in Fig. 4.
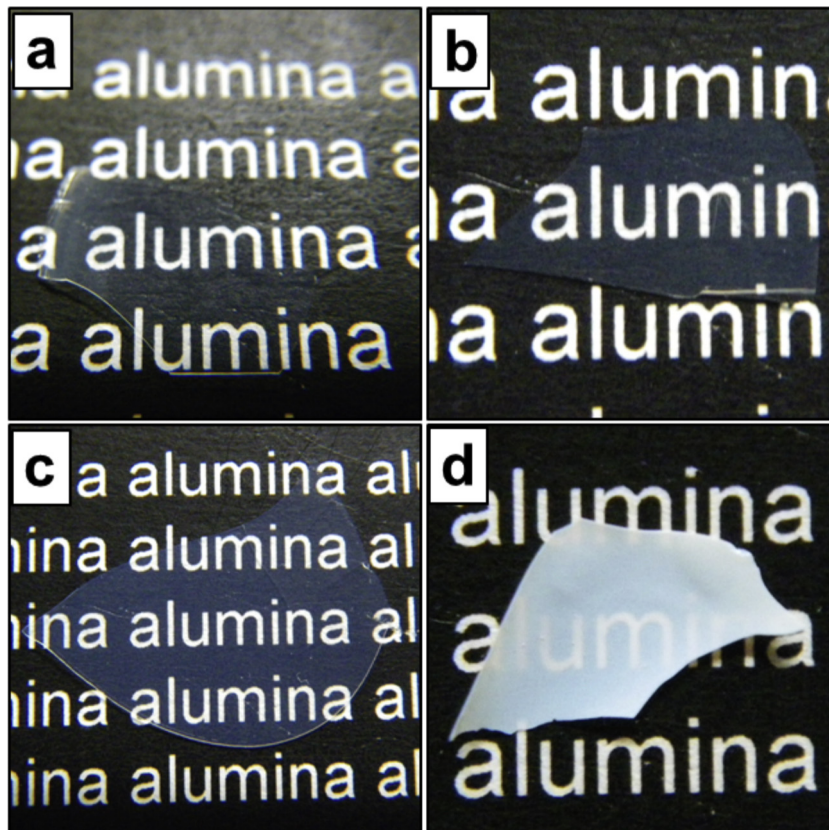

Fig. 4. Photographs of (a) as-prepared alumina gel film and alumina gel films annealed at (b) 300 °C, (c) 900 °C and (d) 1100 °C.
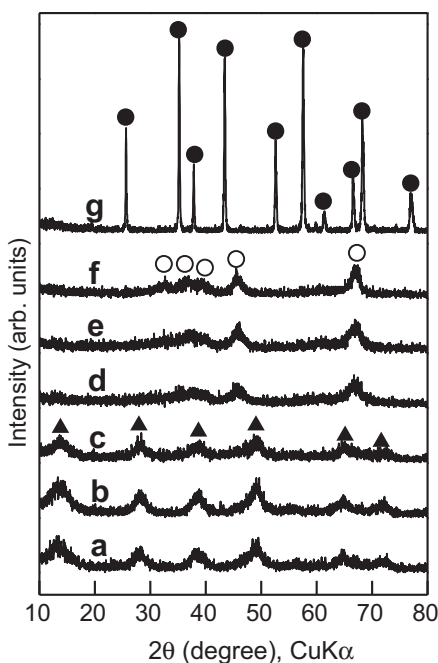
Fig. 5. XRD patterns of (a) as-prepared alumina gel and alumina gels annealed at (b) 100 °C, (c) 300 °C, (d) 500 °C, (e) 700 °C, (f) 900 °C and (g) 1100 °C. ●: α-Al$_2$O$_3$; ○: γ-Al$_2$O$_3$; ▲: boehmite.
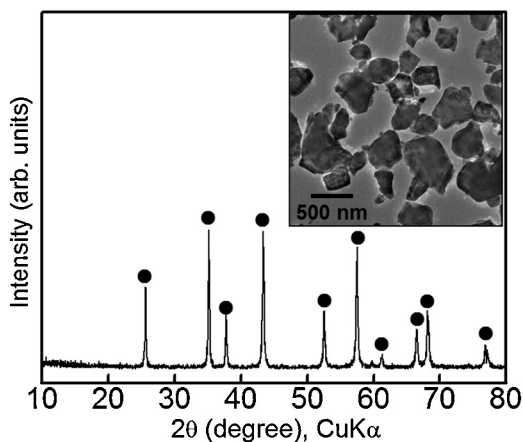

Fig. 6. XRD pattern of particles used as seeds. Inset shows their TEM image. ●: α-Al$_2$O$_3$.

3.3. Alumina gels seeded with α-Al$_2$O$_3$ particles

An inset of Fig. 6 shows a TEM image of the particles used as seeds. The particles were angular in shape and appeared polydispersed; their average size was 389 ± 128 nm. Fig. 6 shows an XRD pattern of the particles; all detected peaks could be attributed to α-Al$_2$O$_3$, which verified that the seeds used were pure α-Al$_2$O$_3$.

Fig. 7(A) shows the XRD patterns of alumina gels seeded with 1 wt% α-Al$_2$O$_3$ particles. The as-prepared seeded alumina gel was boehmite, which became γ-Al$_2$O$_3$ after annealing at 900 °C. This tendency to transform the crystal structure was the same as in the non-seeded alumina gel, as shown in Fig. 5. This result indicated that the 1 wt% seeding did not affect the crystal structure of the alumina gel at the annealing temperature of 900 °C. Fig. 7(B) shows the XRD patterns of the alumina gels seeded with 5 wt% α-Al$_2$O$_3$ particles. For the as-prepared seeded alumina gel, several peaks due to boehmite appeared. A peak assigned to α-Al$_2$O$_3$ was also detected
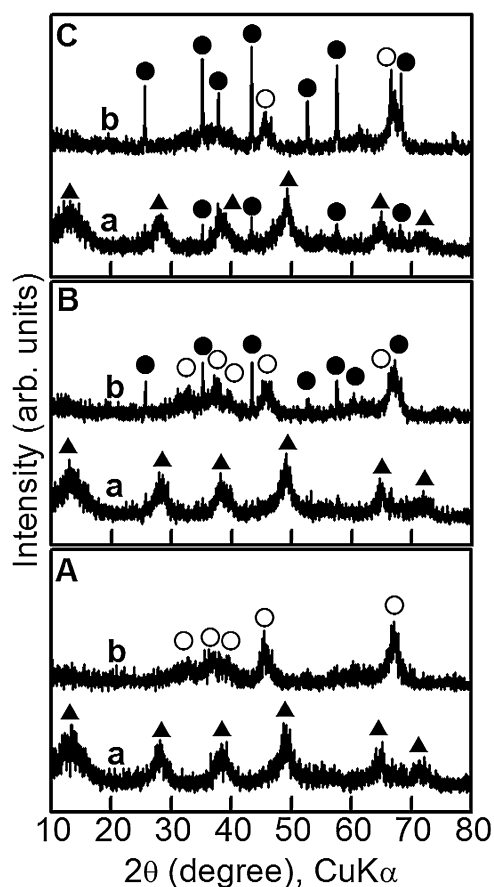

Fig. 7. XRD patterns of alumina gels seeded with (A) 1 wt%, (B) 5 wt% and (C) 10 wt% α-Al$_2$O$_3$ particles. Samples (a) and (b) stand for as-prepared seeded alumina gel and seeded alumina gel annealed at 900 °C. ●: α-Al$_2$O$_3$; ○: γ-Al$_2$O$_3$; ▲: boehmite.

at a low magnitude of ca. 58°, which indicated the presence of α-Al$_2$O$_3$ seed crystallites. In contrast, besides the peaks due to γ-Al$_2$O$_3$, several sharp peaks attributable to α-Al$_2$O$_3$ were detected after the 900 °C annealing, indicating that the 5 wt% seeding promoted the crystallization to α-Al$_2$O$_3$ compared to other contents as small as 1 wt%. The seeding effect on the crystallization of the alumina gel to α-Al$_2$O$_3$ was thus verified with these XRD results. The alumina gel was considered to be crystallized epitaxially on the α-Al$_2$O$_3$ particle surface. Fig. 7(C) shows the XRD patterns of the alumina gels seeded with 10 wt% α-Al$_2$O$_3$ particles. The α-Al$_2$O$_3$ content was so high that several sharp peaks attributable to α-Al$_2$O$_3$ were also detected in addition to the peaks due to boehmite. Their intensities increased with the 900 °C annealing due to the seeding effect.

Fig. 8 shows the intensities of the XRD peaks assigned to α-Al$_2$O$_3$ for the as-prepared seeded alumina gels and for the seeded alumina gels annealed at 900 °C as a function of α-Al$_2$O$_3$ content. The peak intensities were calculated by subtracting background intensities from the measured intensities. For the as-prepared gels, the intensities were 0 cps at 0 and 1 wt%, 48.3 cps at 5 wt% and 81.7 cps at 10 wt%. For the annealed gels, the intensities were still 0 at 0 and 1 wt%, but they reached 58.3 and 198.3 cps at 5 and 10 wt%, respectively. A difference between the intensities between the as-prepared and annealed gels was 116.6 cps at 10 wt%, which was larger than 10.0 cps at 5 wt%. This result indicated that the seeding effect was more dominant at high contents of α-Al$_2$O$_3$. The total apparent surface area of α-Al$_2$O$_3$ particles with a high α-Al$_2$O$_3$ content is larger than that with a low α-Al$_2$O$_3$ content; this large surface area for high α-Al$_2$O$_3$ content provided effective epitaxial
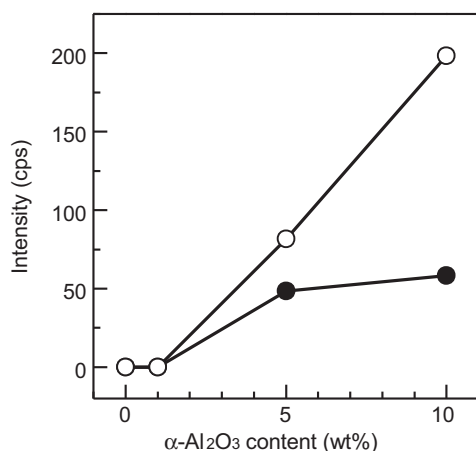
Fig. 8. XRD intensities of α-Al$_2$O$_3$ vs. seed content. ●: as-prepared alumina; ○: alumina annealed at 900 °C.

crystallization compared to the smaller area of low α-Al$_2$O$_3$ content. Consequently, the crystallization to α-Al$_2$O$_3$ was significantly promoted with seeding at higher content.

4. Conclusions

Transparent alumina sol was successfully produced by the peptization of the white product, which was prepared via hydrolysis of aluminum isopropoxide in water, with the addition of acetic acid at 80 °C. Alumina seeded with α-Al$_2$O$_3$ particles was fabricated by drying the sol containing α-Al$_2$O$_3$ particles at room temperature. The non-seeded alumina gel was in the boehmite state even after annealing at 300 °C but became γ-Al$_2$O$_3$ and α-Al$_2$O$_3$ after annealing at 500–900 °C and at 1100 °C, respectively. For the alumina seeded with α-Al$_2$O$_3$ particles, the crystallization of the alumina gel to α-Al$_2$O$_3$ was promoted significantly with increasing α-Al$_2$O$_3$ particle content in the film. The alumina seeded at 5% α-Al$_2$O$_3$ particle content began to crystallize into α-Al$_2$O$_3$ by annealing at temperatures as low as 900 °C.

References

[1] V. Edlmayr, M. Moser, C. Walter and C. Mitterer, Surf. Coat. Technol., 204, 1576–1581 (2010).
[2] Z. Xie, W. Xue, H. Chen and Y. Huang, Ceram. Int., 37, 2165–2168 (2011).
[3] F. Nahif, D. Music, S. Mráz, H. Bolvardi, L. Conrads and J.M. Schneider, Surf. Coat. Technol., 235, 250–258 (2013).
[4] X. Zhang, K. Zhou, X. Wei, B. Chen, J. Song and M. Liu, Ceram. Int., 40, 12703–12708 (2014).
[5] F. Nahif, S. Mráz, D. Music, P. Keuter and J.M. Schneider, Surf. Coat. Technol., 257, 333–337 (2014).
[6] L. Zhu and Q. Huang, Ceram. Int., 37, 249–255 (2011).
[7] G.R. Karagedov and A.L. Myz, J. Eur. Ceram. Soc., 32, 219–225 (2012).
[8] G.C. Cunha, L.P.C. Romão and Z.S. Macedo, Powder Technol., 254, 344–351 (2014).
[9] T. Tanase, A. Nishikata, Y. Iizuka, Y. Kobayashi, M. Konno and T. Miwa, J. Ceram. Soc. Jpn., 110, 911–915 (2002).
[10] T. Tanase, Y. Kobayashi, T. Miwa and M. Konno, Mater. Res. Soc. Symp. Proc., 784, C3.32.1–C3.32.6 (2004).
[11] T. Tanase, Y. Kobayashi, T. Nabatame, T. Miwa and M. Konno, Thin Solid Films, 471, 71–75 (2005).
[12] Y. Kobayashi, Y. Iizuka, T. Tanase and M. Konno, J. Sol-Gel Sci. Technol., 33, 315–321 (2005).
[13] K. Inoue, H. Kurebayashi, M. Hama, Y. Kobayashi, Y. Yasuda and T. Morita, J. Ceram. Soc. Jpn., 121, 494–497 (2013).
[14] K. Inoue, M. Hama, Y. Kobayashi, Y. Yasuda and T. Morita, ISRN Ceram., 2013, 317830 (2013).
[15] M. Sharbatdaran, M.M. Amini and A. Majdabadi, Mater. Lett., 64, 503–505 (2010).
[16] L. Xu, H. Song and L. Chou, Mater. Chem. Phys., 132, 1071–1076 (2012).
[17] J.S. Lee, H.S. Kim, N.-K. Park, T.J. Lee and M. Kang, Chem. Eng. J., 230, 351–360 (2013).
[18] Y. Kobayashi, T. Ishizaka and Y. Kurokawa, J. Mater Sci., 40, 263–283 (2005).
[19] T. Klimova, M.L. Rojas, P. Castillo, R. Cuevas and J. Ramirez, Microporous Mesoporous Mater., 20, 293–306 (1998).
[20] P.K. Sharma, V.V. Varadan and V.K. Varadan, J. Eur. Ceram. Soc., 23, 659–666 (2003).
[21] I.A. Siddiquey, T. Furusawa, M. Sato, N.M. Bahadur and N. Suzuki, Mater. Chem. Phys., 130, 583–586 (2011).
[22] L. Sharifi, M. Beyhaghi, T. Ebadzadeh and E. Ghasemi, Ceram. Int., 39, 1227–1232 (2013).
[23] A. Dey, N. Kayal, A.R. Molla and O. Chakrabarti, Thermochim. Acta, 583, 25–31 (2014).
[24] X. Wu, D. Wang, Z. Hua and G. Gu, Mater. Chem. Phys., 109, 560–564 (2008).
[25] A. Mahapatra, B.G. Mishra and G. Hota, Ceram. Int., 37, 2329–2333 (2011).