Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 3321–3327

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Polymer-network hydrogel facilitated synthesis of Ca-α-SiAlON balls composed of nanoparticles

I. Najafi Hajivar[a], M. Kokabi[b,*]

[a]Nanotechnology Group, Faculty of Engineering, Tarbiat Modares University, P.O. Box 14115-143, Tehran, Islamic Republic of Iran
[b]Polymer Engineering Department, Faculty of Chemical Engineering, Tarbiat Modares University, P.O. Box 14115-114, Tehran, Islamic Republic of Iran

Received 2 August 2012; received in revised form 4 October 2012; accepted 5 October 2012
Available online 12 October 2012

Abstract

In this work, preparation of Ca-α-SiAlON balls composed of nanoparticles with the stoichiometric composition of $Ca_1Si_9Al_3O_1N_{15}$ was successfully developed through a hydrogel route. A polyacrylamide gel embedding nano-silica and dispersed Al^{3+} and Ca^{2+} ions was first dried then calcined under N_2 flow up to 1450 °C for 1 h. Ca-α-SiAlON was formed owing to carbothermal reduction and nitridation (CRN) process, with the polymer acting as carbon source. Due to homogeneity of mixture constituents at molecular level, the soaking time of optimal synthesis condition was reduced to 1 h. In addition, FE-SEM investigation of the resultant powder showed that ball-shaped Ca-α-SiAlON was obtained at 1450 °C after 1 h. It was found that nanoparticles were formed on the surface of the balls after CRN process. Moreover, the ball-milled nanopowder was sintered under N_2 atmosphere by pressureless sintering (PLS). This nitride ceramic exhibits high Vickers hardness (13.5 GPa), proper fracture toughness (4.82 MPa $m^{1/2}$) and a very low specific wear rate (2.49×10^{-4} $mm^3\,N^{-1}\,m^{-1}$) at a contact stress of 5 MPa. All These findings imply that Ca-α-SiAlON ceramics are promising candidate for tribological applications.

Keywords: Ca-α-SiAlON; Polyacrylamide; Tribological properties; Carbothermal reduction and nitridation (CRN) process

1. Introduction

It is well known that SiAlON has two important crystalline forms, i.e., α- and β-SiAlON [1–3]. Between them, α-SiAlON exhibits considerably higher hardness and better oxidation and creep resistances [4,5]. General formula for α-SiAlON is $M_{m/\upsilon}Si_{12-(m+n)}Al_{(m+n)}O_nN_{16-n}$, where υ is the valency of stabilizing cation M which may be Li, Mg, Ca or some rare-earth elements [6]. Low production cost, low residual glassy phase in product owing to high cation solubility (Ca^{2+}) in the α-SiAlON lattice and excellent thermal stability are the main advantages of Ca-α-SiAlON [4,7,8].

In general, α-SiAlON ceramics are produced by sintering of powder mixture of Si_3N_4–AlN–M_xO_y at high temperature through a liquid sintering process [9]. This process usually requires high sintering temperature (1700–2000 °C) and highly pure nitride powders as precursor [9]. This process suffers from several drawbacks such as rigid agglomeration of as-synthesized powder and consequently a post-synthesis grinding step will be needed to pulverize the products [9]. Materials type and kind for synthesis of α-SiAlON powder can be divided into different categories: slag–clay mixture [10], clay–metal compound [11], talc ($Mg_3Si_4O_{10}(OH)_2$)–halloysite clay mineral [7] and carbon containing Ca- or Y-oxide–Al_2O_3–SiO_2 powder mixture [7].

However, except the Hui et al. [9] and Mitomo et al. [12] there have been no reports on the synthesis of pure α-SiAlON powder by wet chemical method. To synthesize Ca-α-SiAlON nanopowder, in this work, polymer/nanosilica/Al^{3+}/Ca^{2+} mixture was used via carbothermal-reduction and nitridation (CRN) process. Three-dimensional (3D) polyacrylamide tangled network plays a double role; (i) providing nano-cavities for metal cations soaking and (ii) preparing carbon atoms that are needed for CRN reaction. Mixture of polymer, colloidal silica, and calcium

---

*Corresponding author. Tel./fax: +98 21 8288 3340.
E-mail address: mehrir@modares.ac.ir (M. Kokabi).

0272-8842/$ - see front matter © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.10.021

and aluminum metal ions at molecular level was helpful to lower the calcination time. This outcome not only provides the possibility of producing fully dense α-SiAlON ceramic but also shows that polyacrylamide gel route is an attracting and alternative method for fabricating wavelength-conversion phosphor such as Eu-doped Ca-α-SiAlON that has been previously produced via mechanochemical method [13].

The main objective of the present work was to synthesis the Ca-α-SiAlON nanopowder via polyacrylamide gel method, and to study the tribological properties of its pressureless sintered ceramic.

2. Experimental

2.1. Materials

In this work, calcium nitrate tetrahydrate, colloidal silica nanoparticles, and aluminum nitrate nonahydrate act as sources of calcium, silicon and aluminum, respectively. The characteristics of these materials are given in Table 1.

2.2. Synthesis of pure Ca-α-SiAlON nanopowder

A homogenous mixture of the quaternary Ca–Si–Al–O system with a target composition of $Ca_1Si_9Al_3O_1N_{15}$ was prepared on the basis of the procedure presented in Fig. 1. According to the stoichiometric coefficients of cations in target material, i.e., $Ca_1Si_9Al_3O_1N_{15}$, the cations sources were dissolved under constant stirring in deionized water until a clear solution was obtained. This solution was then added to the premixed solution of acrylamide (AAm) and N,N′-methylene-bis-acrylamide (Bis) organic monomers. The resultant solution was heated at 80 °C, and free-radical cross-linking copolymerization of AAm and Bis was initiated during addition of freshly made 10% (w/v) (APS) and 1% (v/v) (TEMED) and few minutes later, the solution was converted into hydrogel. The obtained hydrogel was dried at 90 °C for 4 h.

Finally, the formed xerogels was placed in an alumina crucible and calcined in N_2 atmosphere (>99.999% purity) at 1450 °C for 1 h. Any residual carbon was removed by burning the resultant powders at 700 °C for 2 h in air. Hotta and coworkers demonstrated that the maximum Ca-α-SiAlON content occurred with the starting composition $Ca_xSi_{12-3x}Al_{3x}O_xN_{16-x}$ ($x=m/\upsilon=n$) with $x=1.0$ [14]. The same composition was studied in the present work. The expected overall chemical reactions leading to the formation of this composition are presented as follows [14]:

$$xCaO+(12-3x)SiO_2+(1.5x)Al_2O_3+(24-1.5x)C\\+(16-x)/2N_2\rightarrow Ca_xSi_{12-3x}Al_{3x}O_xN_{16-x}+(24-1.5x)CO \quad (1)$$

At the composition of $x=1.0$, Eq. (1) can be rewritten as follows:

$$CaO+9SiO_2+1.5Al_2O_3+22.5C\\+7.5N_2\rightarrow Ca_1Si_9Al_3O_1N_{15}+22.5CO \quad (2)$$

Originated carbon content from burning AAm was fixed at 1.2 folds of the amount required for stoichiometric value according to Eq. (2).

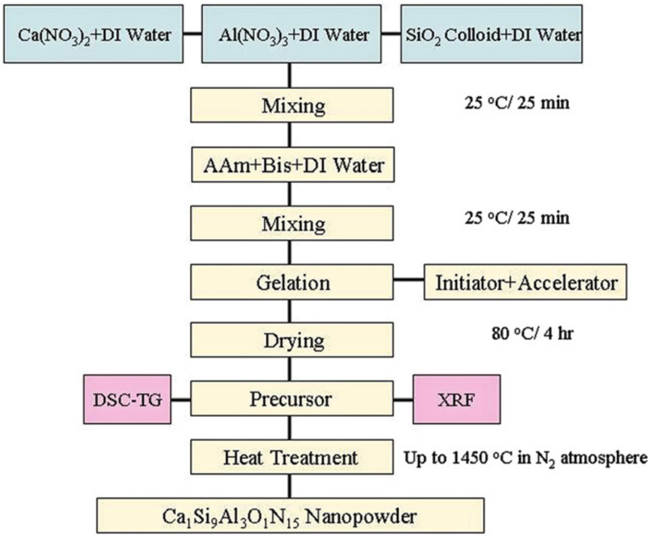

Fig. 1. Flow chart for synthesis of $Ca_1Si_9Al_3O_1N_{15}$ nanopowder by a polyacrylamide gel method.

Table 1
Characteristics of materials.

Materials	Function	Molecular formula	Supplier
Acrylamide (AAm)	Monofunctional monomer	$C_2H_3CONH_2$	Merck[a]
N,N′-Methylene bis acrylamide (Bis)	Difunctional monomer (crosslinker)	$(C_2H_3CONH_2)CH_2$	Merck[a]
Ammonium persulfate (APS)	Initiator	$(NH_4)S_2O_8$	Merck[a]
N,N,N′,N′-Tetramethyl ethylene diamine (TEMED)	Accelerator	$C_6H_{16}N_2$	Merck[a]
Aluminum nitrate nonahydrate	Aluminum source	$Al(NO_3)\cdot 9H_2O$	Sigma-Aldrich[b]
Calcium nitrate tetrahydrate	Calcium source	$Ca(NO_3)\cdot 4H_2O$	Sigma-Aldrich[b]
Colloidal silica	Silicon source	SiO_2	Sigma-Aldrich[b]

[a] E. Merck, D 6100 Darmstadt, Germany.
[b] St. Louis, USA.

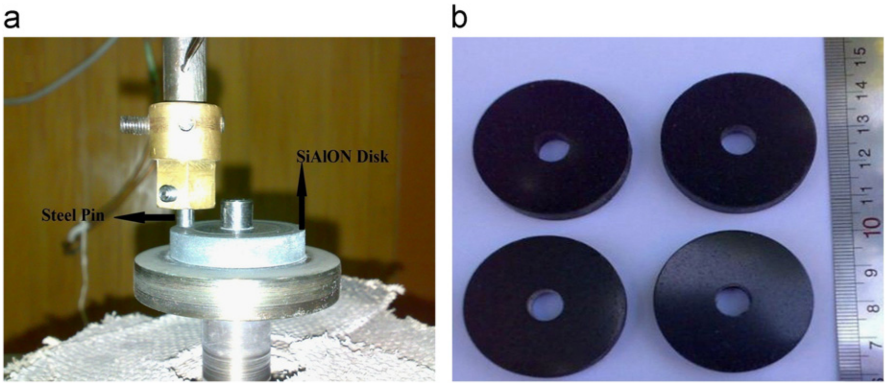

Fig. 2. Images of: (a) pin-on-disk tests of Ca-α-SiAlON ceramic and (b) sintered and polished SiAlON samples.

2.3. Sample preparation and tribological test procedure

A ceramic disk of α-SiAlON was pressureless-sintered in a nitriding furnace (KCE, Germany) with a nitrogen flow rate of 3 L min^{-1}. The sintering temperature was fixed at 1500 °C and the soaking time at sintering temperature was 3 h. For tribological investigation, a home-made pin-on-disk machine equipped with a computer was used to evaluate friction and wear behavior of α-SiAlON/steel pair according to ASTM G99. α-SiAlON disk with thickness and diameter of 8 and 35 mm, respectively was ground and polished to a mean surface roughness of 14 μm and then was fixed onto an rotating disk (Fig. 2). DIN CK45K steel pin with 5 mm in diameter was fixed to a load arm with chuck. The steel pin presents a hardness value of 230 HB.

Normal applied load on the steel pin was provided by a pneumatic system with a compression load cell and a piezoelectric sensor was used to measure the friction force. Pin and disk were washed by acetone and the experiments were performed with a contact stress of 5 MPa (100 N normal load) and a sliding speed of 0.5 m s^{-1} for 1000 m of sliding distance. In order to eliminate any lubricant contribution, the test was carried out at room temperature ($\approx$22 °C) with a relative humidity of about 50%. Specific wear rate (K_w) was calculated by the following equation:

$$K_w = \frac{\Delta V}{Fd} \tag{3}$$

where ΔV is the lost volume (mm^3), d is the sliding distance (m) and F is the normal applied load (N).

2.4. Characterization

Crystalline structure of resulting Ca-α-SiAlON nanopowders was characterized by X-ray diffraction (XRD) (Philips pw3710, The Netherlands, with Cu-Kα_1 radiation, λ=0.15406 nm). Morphology was observed with FE-SEM (S-4700, Japan, 15.0 kV) and TEM (Zeiss, EM-10C, Germany, 100 kV).

The doped xerogels with Al^{3+} and Ca^{2+} ions and colloidal silica were studied by thermal analysis (DSC–TGA, STA 409 PC/PG, Netzsch, Germany). These thermal analyses were performed from ambient temperature to 700 °C with a heating rate of 10 °C min^{-1} in N$_2$ atmosphere. X-ray fluorescence (XRF) analysis was used to measure the precursor stoichiometry. Density of sintered sample was measured according to Archimedes water-displacement method. Vickers indentation (H_v) was used to measure the hardness of the sintered disk. Measurement conditions were as follows: applied load of 100 N and loading time of 10 s. Indentation fracture toughness, (K_{1C}), at room temperature was also calculated by measuring the lengths of the four cracks emerging from the corners of each indentation according to the equation given by Li et al. [15].

3. Results and discussion

3.1. Thermal analysis

It is known that monomers precursors included AAm and Bis copolymerize during an exothermic process, through passing from monomer state to three-dimensional network. As shown in Fig. 3, it is highly probable that polymer fragments such as amine (NH$_2$) groups retained bonding with Al^{3+} and Ca^{2+} ions through hydrogen bonding with unshared electron pairs on nitrogen atoms. These ions and nanosilica which are coordinated with amine groups, are trapped within hydrogel pores.

Typical TGA and DSC curves of the xerogels, doped with Al^{3+} and Ca^{2+} ions and colloidal silica are presented in Fig. 4. TGA curve in Fig. 4 shows a weight loss of 83.5% from ambient temperature to 700 °C which can be attributed to dehydration of the precursors, decomposition and removal of polymer fragments, nitrates, etc. Weak endothermic peak associated with a weight loss of about 16% at temperatures below 250 °C, belongs to the removal of physically absorbed water molecules. The second step weight losses at about 250–700 °C mainly corresponds to the oxidative removal of organic and polymer fragments. The nitrates (oxidants) react with polymer network (reductant) and accelerate its degradation [16]. Since redox reaction involving nitrates, ammonium persulfate and polymer fragments is an exothermic reaction, two exothermic peaks are observed at about 380 °C and 530 °C

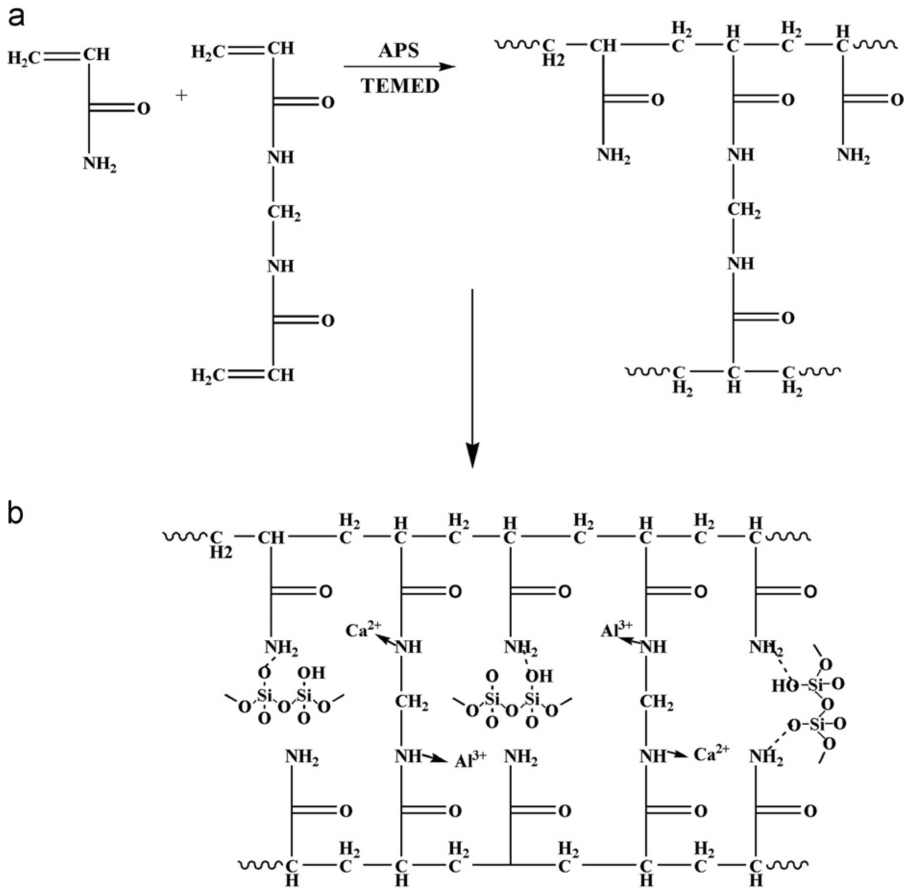

Fig. 3. Preparation of: (a) polyacrylamide hydrogel and (b) trapped and coordinated ions in hydrogel pores.

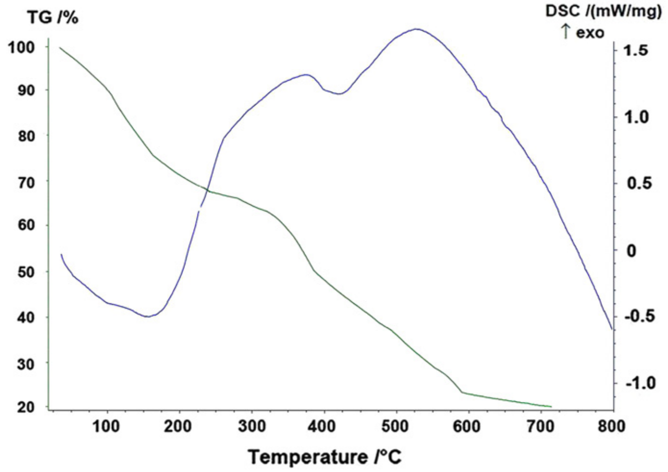

Fig. 4. DSC–TGA curve of xerogels doped with Al^{3+} and Ca^{2+} ions and colloidal silica heated up to 700 °C under N_2 atmosphere.

and polymer network degradation completes at temperature about 600 °C.

3.2. *Polymer–salts reactions and formation of mixed oxides in $Ca_1Si_9Al_3O_{23.5}$ system*

For xerogels combustion, a redox reaction between nitrate salts and polymer network can be proposed. This combustion reaction releases large amount of gases consisted of CO, CO_2, H_2O and N_2. The stoichiometry of the redox mixture used for combustion was calculated using the total oxidizing valences of the components [17]. The valence sign of the oxidizing element, i.e., oxygen has been considered as negative and those of the fuel elements, i.e., C and H regard as positive, whereas that of N is taken as null [18]. According to this assumption, the valences of $C=+4$, $H=+1$, divalent metal ions $=+2$, trivalent metal ions $=+3$, $O=-2$ and $N=0$. In this work, AAm (C_3H_5NO) and Bis ($C_7H_{10}N_2O_2$) with molar ratio of 10/1 were used to make hydrogel. Therefore, the total reducing valences of fuels (*TVF*) can be calculated as follows:

$$TVF = 1\times((3\times4)+(5\times1)+(1\times(-2)))+0.1\times((7\times4)+(10\times1)+(2\times(-2))) = 18.4 \tag{4}$$

Aluminum nitrate and calcium nitrate with molar ratio of 3/1 are containing oxidizing agent, thus total oxidizing valences of oxidizer (*TVO*) can be calculated as follows:

$$TVO = (3-18)+0.33\times(2-12) = 18.3 \tag{5}$$

Magnitudes of the total reducing and oxidizing valences serve as numerical coefficient for the oxidizer and the fuels, respectively, in stoichiometric balance [18]. To assume completely oxidized products, one can write the stoichiometry balanced equation as follows:

$$18.3C_3H_5NO+1.83C_7H_{10}N_2O_2+18.4Al(NO_3)_3 +6.13Ca(NO_3)_2+55.17SiO_2\rightarrow 6.13Ca_1Si_9Al_3O_{23.5} +67.71CO_2+54.9H_2O+44.71N_2 \quad (6)$$

The obtained mixed oxides converted to $Ca_1Si_9Al_3O_1N_{15}$ nanopowders according to the following equation:

$$6.13Ca_1Si_9Al_3O_{23.5}+137.925C +45.975N_2\rightarrow 6.13Ca_1Si_9Al_3O_1N_{15}+137.925CO \quad (7)$$

Considering these reactions in polymer–salts systems and thermal analysis of precursors are helpful to appraise the amount of monomers that facilitate carbon for CRN process according to the Eq. (7). Moreover, results of the XRF analysis of the as-prepared precursor after heat treatment up to 700 °C in N_2 atmosphere are shown in Table 2. It is appeared that product has correct stoichiometry.

3.3. Crystallization

Fig. 5 provides XRD patterns of the calcined products at 1450 °C and held at zero and 1 h in soaking time. As shown in Fig. 2a, only a broad hump can be observed at low 2θ angles which could be attributed to the existence of an amorphous phase containing Ca–Si–Al–O quaternary elements. It is noteworthy to mention that, with respect to the precursors used to synthesize Ca-α-SiAlON nanopowder, Si–Al–Ca–O liquid phase can be formed above the $CaO–Al_2O_3–SiO_2$ eutectic temperature of 1170 °C [7]. The amount of this liquid phase increases further with increasing temperature [19]. This liquid amorphous phase solidified on cooling and presents itself as a broad hump in XRD pattern.

Table 2
The XRF elemental analysis of as-prepared precursor.

Oxide and carbon	Stoichiometric	Measured
CaO	5.49	6.02
Al_2O_3	15.01	16.05
SiO_2	52.99	50.41
C	26.50	27.47

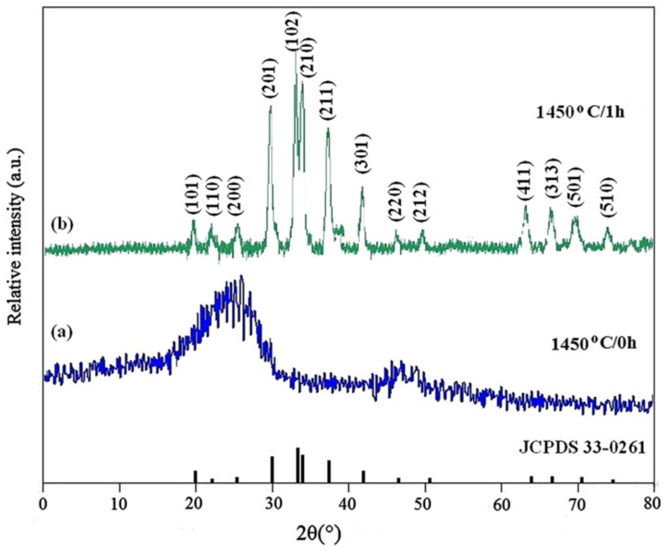

Fig. 5. X-ray diffraction patterns of the calcined products at 1450 °C in different soaking times: (a) 0 h and (b) 1 h.

As it is observed in Fig. 2b, well-crystallized pure Ca-α-SiAlON nanopowder (JCPDS 33-0261) was successfully synthesized at 1450 °C after 1 h. In this work, polyacrylamide network was selected as carbon source in comparison with previous reported carbothermal reduction and nitridation (CRN) methods [7,20].

3.4. Particle size and morphology

FE-SEM micrographs of precursor and Ca-α-SiAlON balls (1450 °C, 1 h) are shown in Fig. 6. The precursor exhibited a uniform and highly agglomerated morphology because of using three-dimensional polyacrylamide network. The synthesized Ca-α-SiAlON powders has a ball-like morphology of 100–1000 nm in diameter. Also, a high-magnification FE-SEM and TEM micrographs of Ca-α-SiAlON balls are shown in Figs. 6c and 7a, respectively.

It was found that nanoparticles were formed and covered the surface of the aforementioned balls at the final stage of CRN process. The as-prepared Ca-α-SiAlON powders were ball-milled (30 min in a planetary ball milling), in order to grind the balls into a well-dispersed and nanosized particles. Ca-α-SiAlON nanoparticles with equiaxial morphology were obtained as is observed in TEM micrograph of Fig. 7b. The average particle size was about 30–60 nm. Formation of spherical particles could be attributed to Ca–Si–Al–O liquid phase that formed above the $CaO–Al_2O_3–SiO_2$ eutectic temperature (1170 °C) [7]. High viscosity and high surface tension are two characteristics of the Ca–Si–Al–O liquid phase. These characteristics lead to ball formation. With increasing temperature, the polymer plays a dual role; (i) acts as reducing agent in CRN process and (ii) increases surface tension of Ca–Si–Al–O liquid phase via a covering layer. With increasing temperature, the interfacial tension between liquid and covered carbon decreased and simultaneously nitrogen diffused to the liquid and increased the viscosity again. Consequently, the sphericity of the particles remained unchanged [7]. Such morphology and formation mechanism of Ca-SiAlON balls was previously reported by Hotta et al. [6,7,20].

3.5. Properties and tribological performance of sintered disk

Table 3 shows the density and mechanical properties of Ca-α-SiAlON ceramic. Our results demonstrate that ball-milled Ca-α-SiAlON nanopowder nearly densified during single step pressureless sintering process at relatively low

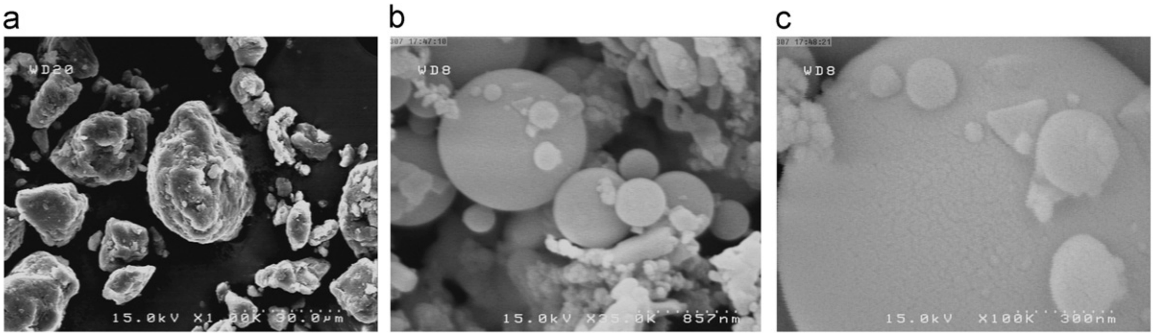

Fig. 6. SEM micrographs of: (a) precursor, (b), and (c) product fired at 1450 °C for 1 h.

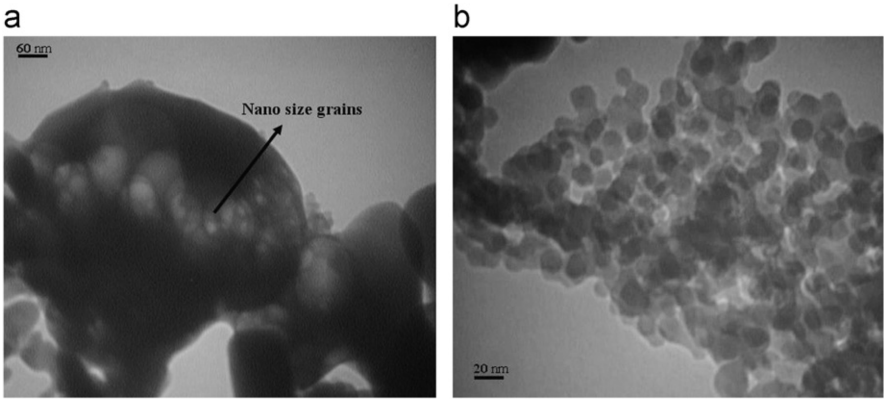

Fig. 7. TEM micrographs of: (a) Ca-α-SiAlON balls composed of large numbers of nanoparticles and (b) after a short grinding (30 min in a planetary ball milling).

Table 3
Density and mechanical properties of Ca-α-SiAlON body.

Advanced ceramic	Density (g cm^{-3})	Hardness[a] (GPa)	Fracture toughness[a] (MPa m$^{1/2}$)
Ca-α-SiAlON	3.078	13.5 ± 0.37	4.82 ± 0.18

[a] Average of ten tests.

temperature (1500 °C/3 h) compared with the two-steps hot-pressing sintering (TSS) procedure reported by Xie et al. [21].

Fig. 8 shows the friction signal and the friction coefficient of Ca-α-SiAlON/steel pair as a function of sliding distance. With increasing sliding distance, the wear debris formed and then agglomerated in the interface of ceramic/steel pair due to increase of tangential force at the interface. Consequently, the friction signal increases. Weight loss, friction coefficient and specific wear rate of Ca-α-SiAlON reported in Table 4. The specific wear rate (K_w) of Ca-α-SiAlON at contact stress of 5 MPa was measured to be 2.49×10^{-4} mm^3 N^{-1} m^{-1} which is higher than the specific wear rate value (2.33×10^{-6} mm^3 N^{-1} m^{-1}) of yttrium-stabilized α-SiAlON at contact stress of 2.85 MPa reported by Reis et al. [22]. These results demonstrate that calcium stabilized SiAlON ceramic presents better performance under dry sliding wear conditions which makes it a promise candidate for several tribological applications such as: mechanical seals, cutting tools and high efficiency engines.

4. Conclusion

In summary, we innovate a convenient and effective polyacrylamide hydrogel method to synthesize pure Ca-α-SiAlON nanopowders using polymer/nanosilica/Al^{3+}/Ca^{2+} mixture as a new precursor. Polymer hydrogel network plays a dual role; (i) provides nano-cavities for soaking of metal cations and (ii) acts as pure carbon source needed for CRN reaction. By this method, the CRN reaction was completed at 1450 °C and 1 h soaking time. In addition, the ball-milled nanopowders show good sintering ability (1500 °C/3 h) and the obtained Ca-α-SiAlON ceramic presents proper mechanical properties and tribological performance. In a word, polyacrylamide hydrogel method can be addressed as a reliable process for producing Ca-α-SiAlON

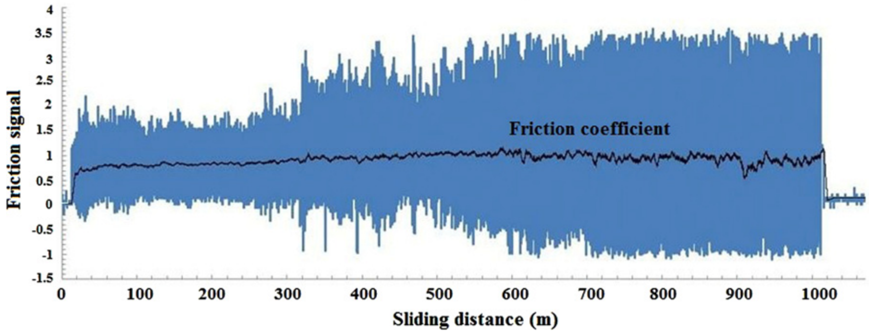

Fig. 8. Plot of friction versus sliding distance.

Table 4
Weight loss, friction coefficient and specific wear rate of Ca-α-SiAlON body.

Advanced ceramic	Weight loss (Δm) (mg)	Friction coefficient (μ)	Specific wear rate K_w ($mm^3\ N^{-1}\ m^{-1}$)
Ca-α-SiAlON	39.3	0.87	2.49×10^{-4}

nanopowders with high purity and the corresponding sintered ceramic parts are promising candidates for tribological applications.

Acknowledgment

The authors would like to thank Tarbiat Modares University and Iran Nanotechnology Initiative Council (INIC) for their supports of this work.

References

[1] G.Z. Cao, R. Metselaar, α′-SiAlON ceramics: a review, Chemistry of Materials 3 (1991) 242–252.

[2] P.L. Wang, C. Zhang, W.Y. Sun, D.S. Yan, Characteristic of Ca-α-SiAlON phase formation, microstructure and mechanical properties, Journal of the European Ceramic Society 19 (1999) 553–560.

[3] J.W.T. Rutten, R.A. Terpstra, J.C.T. van der Heijde, H.T. Hintzen, R. Metselaar, Carbothermal preparation and characterization of Ca-α-SiAlON, Journal of the European Ceramic Society 15 (1995) 599–604.

[4] C. Zhang, E. Narimatsu, K. Komeya, J. Tatami, T. Meguro, Control of grain morphology in Ca-α-SiAlON ceramics by changing the heating rate, Journal of Materials Letters 43 (2000) 315–319.

[5] Y.W. Li, L.P. Wang, W.W. Chen, B.Y. Cheng, D.S. Yan, Effect of processing on toughness of Ca-α-SiAlON ceramics, Journal of Materials Science 35 (2000) 5817–5821.

[6] K. Komeya, C. Zhang, M. Hotta, J. Tatami, T. Meguro, Hollow beads composed of nanosize Ca-α-SiAlON grains, Journal of the American Ceramic Society 83 (2000) 995–997.

[7] M. Hotta, J. Tatami, K. Komeya, C. Zhang, T. Meguro, Formation process of Ca-α-SiAlON hollow balls composed of nanosized particles by carbothermal reduction–nitridation, Journal of the American Ceramic Society 91 (2008) 860–864.

[8] C.L. Hewett, Y.B. Cheng, B.C. Muddle, M.B. Trigg, Thermal stability of Ca-α-SiAlON ceramics, Journal of the European Ceramic Society 18 (1998) 417–427.

[9] L. Hui-Li, N. Hirosaki, R.J. Xie, T. Suehiro, M. Mitomo, Fine yellow α-SiAlON: Eu phosphors for white LEDs prepared by the gas-reduction–nitridation method, Science and Technology of Advanced Materials 8 (2007) 601–606.

[10] Y.B. Cheng, M.R. Terner, W.W. Chen, P.L. Wang, Slag derived α-SiAlON ceramics and their properties, Key Engineering Materials 264–268 (2004) 781–786.

[11] T. Ekstrom, Z.J. Shen, K.J.D. Mackenzie, I.W.M. Brown, G.V. White, α-SiAlON ceramics synthesized from a clay precursor by carbothermal reduction and nitridation, Journal of Materials Chemistry 8 (1998) 977–983.

[12] M. Mitomo, M. Takeuchi, M. Ohmasa, Preparation of α-SiAlON powders by carbothermal reduction and nitridation, Ceramics International 14 (1988) 43–48.

[13] X. Xu, J.Y. Tang, T. Nishimura, L. Hao, Synthesis of Ca-α-SiAlON phosphors by mechanochemical activation route, Acta Materialia 59 (2011) 1570–1576.

[14] M. Hotta, J. Tatami, K. Komeya, T. Meguro, Y.B. Cheng, Effect of starting composition and carbon content on the formation of Ca-α-SiAlON powders by carbothermal reduction–nitridation, Journal of the Ceramic Society of Japan 118 (2010) 827–829.

[15] Z. Li, A. Ghosh, A.S. Kobayashi, R.C. Bardat, Indentation fracture toughness of sintered silicon carbide in the Palmqvist crack regime, Journal of the American Ceramic Society 72 (1989) 904–911.

[16] A.A. Ostroushko, Y.V. Mogilnikov, I.P. Ostroushko, Synthesis of molybdenum and vanadium-containing mixed oxides in polymer–salt systems, Journal of Inorganic Materials 36 (2000) 1256–1263.

[17] T. Chandrappa, S. Ghosh, K.C. Patil, Synthesis and properties of Willemite, Zn_2SiO_4 and M^{2+}:Zn_2SiO_4 (M = Co and Ni), Journal of Materials Synthesis and Processing 7 (1999) 273–279.

[18] S.R. Jain, K.C. Adiga, A new approach to thermochemical calculations of condensed fuel-oxidizer mixtures, Journal of Combustion and Flame 40 (1981) 71–79.

[19] K. Chen, H. Jin, M. Oliveira, H. Zhou, J.M.F. Ferreira, Microstructure and formation mechanism of combustion-synthesized rodlike Ca-α-SiAlON crystal, Journal of Materials Research 16 (2001) 1928–1934.

[20] M. Hotta, J. Tatami, C. Zhang, K. Komeya, T. Meguro, M.R. Terner, Y.B. Cheng, Ca-α-SiAlON hollow spheres prepared by carbothermal reduction–nitridation from different SiO_2 powders, Ceramics International 36 (2010) 1553–1559.

[21] Z.H. Xie, M. Hoffman, Y.B. Cheng, Microstructural tailoring and characterization of a Ca-α-SiAlON composition, Journal of the American Ceramic Society 85 (2002) 812–818.

[22] P. Reis, J.P. Davim, X. Xu, J.M.F. Ferreira, A note on tribological behavior of α-SiAlON/steel couples under dry conditions, Materials and Design 28 (2007) 1343–1347.