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Alon-based materials prepared by SHS technique

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Abstract

The aim of the presented paper was preparation of the highly reactive in the sintering powders in the Al–O–N system by SHS method. Combustion reactions of metallic aluminium and corundum powder mixtures (from 15% Al–85% Al_2O_3 to 50% Al–50% Al_2O_3) were performed in nitrogen atmosphere. The obtained powders were ground and hot-pressed at 1750, 1850 and 1950 °C for 1 h under 25 MPa in nitrogen flow. In contrast to conventional methods, which require 24 h of the precursor heat treatment at 1200 °C our studies, showed that it is possible to prepare almost pure γ-alon materials using SHS reaction. Sintering of the powders led to obtained dense materials composed of pure γ-alon or γ-alon–AlN composites. The phase composition of the sintered bodies was controlled by the chemical composition of the starting mixture and the sintering temperature.

Keywords: SHS synthesis

1. Introduction

Materials based on polycrystalline γ-alon—the solid solution of Al_2O_3 and AlN with spinel structure,[1] have great potential application as high-performance structural ceramics. Since the 1960s, many investigations have been focused on electrical, chemical, mechanical and especially on optical properties of γ-alon materials.[2–9] Alon powders were usually synthesized by direct solid-state reaction between aluminium oxide and aluminium nitride in pure nitrogen or vacuum.[1,6] This reaction, often in multi-stage regime, was performed at relatively high temperature (1200 °C) and long, at least 24 h, time. Direct synthesis of γ-alon from aluminium nitride and oxide mixture took place faster using arc induced plasma.[10]

Another method for γ-alon preparation was carbothermal nitridation of aluminium oxide proposed by Yamaguchi and Yanagida.[11] The substrate mixtures of corundum and carbon black were reacted in pure nitrogen atmosphere at 1700 °C. Modifications of this method were usually connected with changes of precursors (inorganic aluminium salts, starch) and respective reaction conditions.[12–16]

Combustion of metallic aluminium powder in air was proposed by Bouriannes et al.[17] The reaction of inductively heated powder was performed at 1500 °C and gave multiphase product composed of γ-alon, aluminium nitride and corundum. More simple and relatively novel method for γ-alon preparation was described by Gromov et al.[18] In this case, the mixtures with different proportion of metallic aluminium and fine γ-alumina powders were ignited in air. The authors reported that combustion of the mixtures led to product composed of near pure γ-alon.

Alon powders prepared via high-temperature synthesis are usually strongly agglomerated and required intensive grounding before densification. Additionally, some oxide additions (e.g. CaO, MgO or Y_2O_3) are necessary as the sintering aids.[19] These sintering aids form a transient liquid phase, resulting in the promotion of liquid phase sintering during the early sintering stage.[19] Sintering can be also connected with partially synthesis reaction; in this case addition of Al_2O_3 powder is used. Densification of γ-alon powders is usually conducted at relatively high temperatures over 1700 °C, even at 2050 °C. It is due to relatively low diffusion coefficient of alon components[20] and an evaporation–condensation mechanism governs during an initial densification stage.[21]

The aim of the present paper is detail study of alon-based materials preparation by combustion of aluminum and corundum powders mixtures in nitrogen using combustion technique in the self-propagating high-temperature synthesis (SHS) regime. The powders have been tested as the precursors for obtaining dense polycrystalline materials by pressureless sintering and hot-pressing.

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2. Experimental

Metallic aluminium (pure grade: 99.5%) and α-aluminium oxide (MA 250/5 Alcan Chemicals Europe) powders were used as the substrates. Average grain size of the powders was about 3 and 0.5 μm for Al and Al_2O_3, respectively. The powders were mixed for 2 h in propanol using ball mill and zirconia grinding media. Weight proportions between the substrates were established from 15% Al–85% Al_2O_3 to 50% Al–50% Al_2O_3 with 5% interval. The mixtures with weight of 50 g. were poured into graphite crucible in a form of a loose bed and placed into steel water-cooled reactor. The reactor was vacuumed and filled twice with pure (99.8%) nitrogen of 2.5 MPa pressure. The combustion synthesis was initialized by electrical pre-heating of the graphite crucible by electric current flow for several seconds. The combustion got start rapidly, the reaction mixture reached temperature exceeded 2000 °C in few second and after next about 60 s the reaction was completed. The synthesized powders were crushed and then ground in dry propanol for 8 h using rotary–vibratory mill and silicon nitride grinding media. Dried and granulated powders were hot-pressed at 1750, 1850 and 1950 °C for 1 h under 25 MPa in nitrogen flow.

The compacts prepared by cold pressing under 150 MPa were used to characterize densification behaviour of the powders. Changes of the linear shrinkage were investigated by graphite dilatometer up to 1950 °C with temperature progress of 15 °C min^{-1} in pure nitrogen flow.

Morphology of the powders and sintered bodies was observed under scanning microscopy (JEOL, JSM-5400). Phase composition of the powders and sintered samples was described by X-ray diffraction analysis (X'Pert Pro, Philips) and the Rietveld refinement allowed determining the quantitatively phase content. Specific surface area was measured by the nitrogen adsorption using the four-point BET isotherm (ASAP model 2010, Micromeritics). Mercury porosimetry (Carlo-Erba Instruments 2000) allowed determine a pore size distribution in the prepared powders. Apparent density of the sintered samples was calculated basis on the Archimedes method.

3. Results and discussion

It was observed that pre-heating of the Al–Al_2O_3 mixtures in nitrogen atmosphere contained more than 15 wt.% of Al involved strong exothermic SHS reaction accompanied by bright radiation and fast increase of temperature. The measured maximum temperature of the reaction was higher than 2000 °C.

SEM observations (Fig. 1) show that SHS prepared powders are composed of agglomerates being grains of about several hundreds micrometers in size. The agglomerates are formed by much smaller, a few micrometers, particles, probably crystallites, with different shapes. As it is shown in micrographs (Fig. 1b) the particles have elongated, needle- or plate-like shapes what can suggest the vapour–solid and/or vapour–liquid–solid mechanism of their formation. Local EDS measurements revealed chemical inhomogeneity of the powders what suggested presence of different phases.

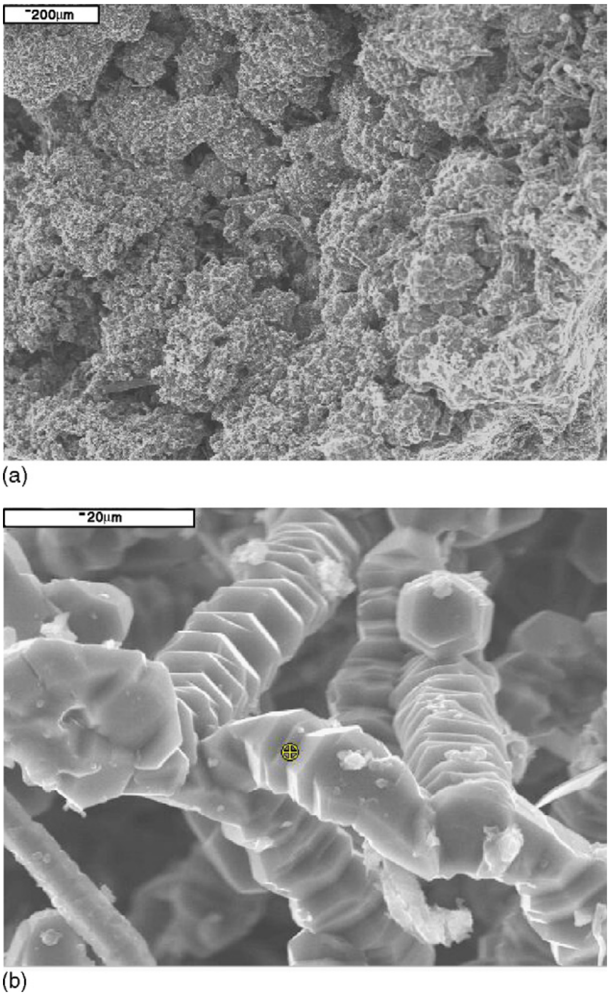

Fig. 1. Morphology of the powder prepared by the SHS method from the mixture of 20% Al and 80% Al_2O_3.

Fig. 2 presents changes of the phase composition of the powders prepared in the combustion mode. X-ray diffraction analysis shows that the powders are multiphase and composed of hexagonal aluminium nitride (AlN), rhombohedral aluminium oxyni-

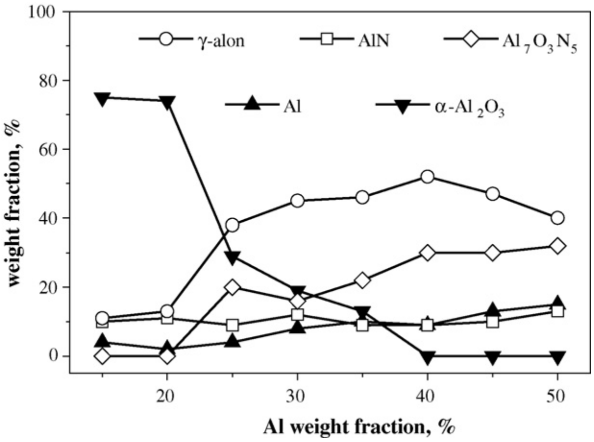

Fig. 2. Phase content of the SHS-derived powders in the Al_2O_3–AlN system vs. Al weight content in the starting reaction mixture.

tride (21R–$Al_7O_3N_5$), γ-alon (Al_3O_3N) and non-fully reacted corundum and aluminium. The phase content is strictly connected with the quantitative composition of the starting SHS mixture. The sizes of the markers in Fig. 2 correspond to the standard deviation of the measurements.

Compositional dependence of the weight fraction of aluminium oxynitrides reach maximum for different content of aluminium in the starting mixtures. Range of the maximum content of γ-alon corresponds to 30–40%, whereas $Al_7O_3N_5$ to 40–60% of aluminium. Taking into account that γ-alon has stoichiometry close to $Al_{23}O_{27}N_5$, it means that the higher aluminium content in the starting mixture lower an aluminium to nitrogen molar ratio. Increase of the aluminium content in the starting mixture corresponds to the small increase of the metal rest in the products of SHS synthesis and simultaneously, increase of aluminium nitride amount can be observed. It suggests direct chemical reaction between aluminium and nitrogen with formation of AlN. The presence of essential amount of residual aluminium oxide in the SHS product is revealed only in the case of starting mixtures with the major content of α-Al_2O_3 (85 and 80%) Significant decrease of alumina in the resulting powders prepared from the mixtures with less content of Al_2O_3 is connected with formation of oxynitride phases. Most probably reason of such behaviour is secondary reaction between aluminium oxide and AlN.

After followed milling, the powders have a specific surface area on a level of about $3\,m^2\,g^{-1}$ what means that respective grain size equals about 0.6 μm. Comparison of this value with the grain size estimated from SEM micrographs (see Fig. 1) indicates on effective breaking of big agglomerates during ground process that is corroborates by porosimetry measurement. Typical pore size distribution in compact made of ground powder shown in Fig. 3.

Fig. 4 presents dilatometric curves taken from the powders pressureless sintered from precursor with different compositions. In each case, the shrinkage behaviour reveals two stages of the sintering process and such effect is much stronger in the sample with relatively bigger amount of the residual aluminium. This is probably connected with additional chemical reactions taking place during densification. The experiments also show that pressureless sintering does not lead to full densification, even at 1950 °C.

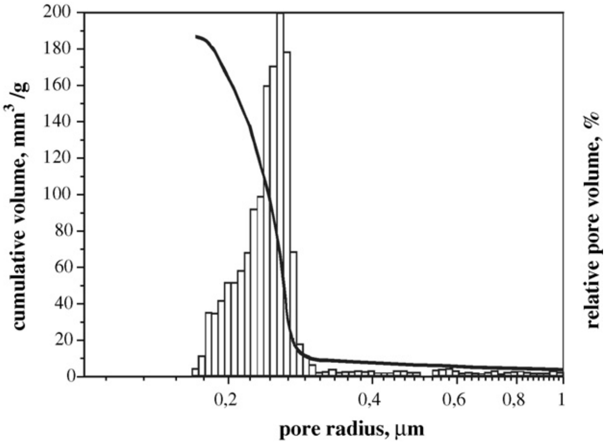

Fig. 3. Pore size distribution in the compacted powder.

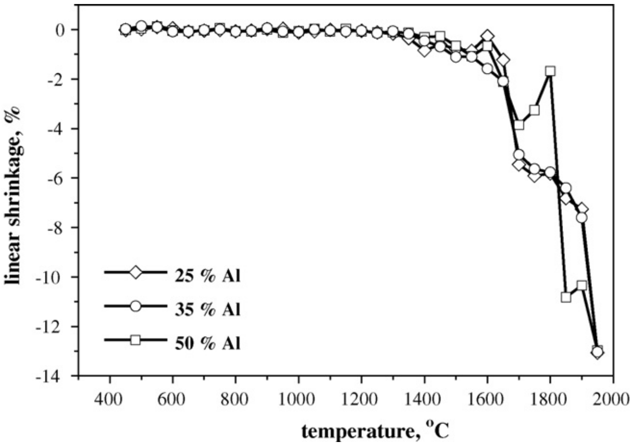

Fig. 4. Dilatometric curves of SHS-derived powders prepare using different Al content in the starting mixtures.

All sintered materials are finally composed mainly of two phases: γ-alon and aluminium nitride. Different phase compositions of the hot-pressed samples also confirm assumption on chemical reaction (Fig. 5). Small amounts of aluminium and $Al_7O_3N_5$ alon, no more than 2% of each one, are also detected.

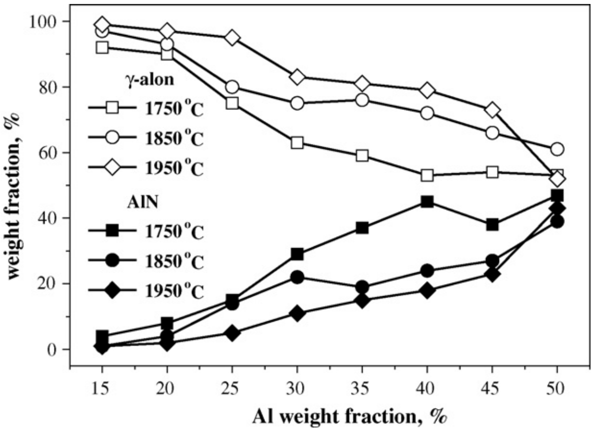

Fig. 5. Phase compositions of the samples hot-pressed at indicated temperatures.

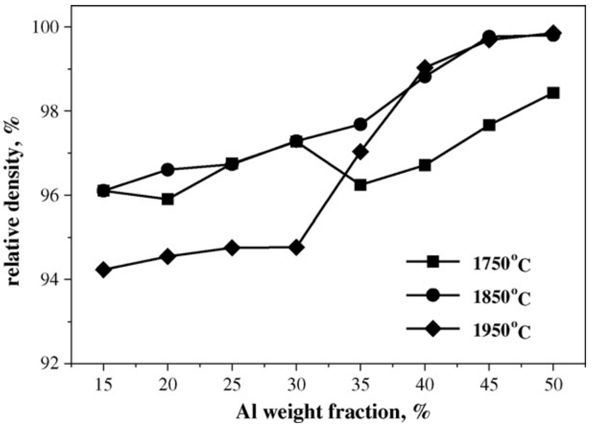

Fig. 6. Relative densities of the samples hot-pressed at different temperatures vs. Al content in the starting SHS mixtures.

Phase composition of the sintered materials depends both on phase composition of the powders and on the temperature. The content of γ-alon decreases with the aluminium content in the starting mixture, whereas changes of the AlN amount have an opposite tendency—it increases with Al content. Increase of the hot-pressing temperature leads to the increase of γ-alon content and decrease of aluminium nitride. It is worth to notice that almost pure γ-alon samples originated from the powder with the highest content of aluminium oxide. Absence of the corundum in the sintered samples reveals on chemical reaction between Al_2O_3 and AlN during densification process (see Fig. 2).

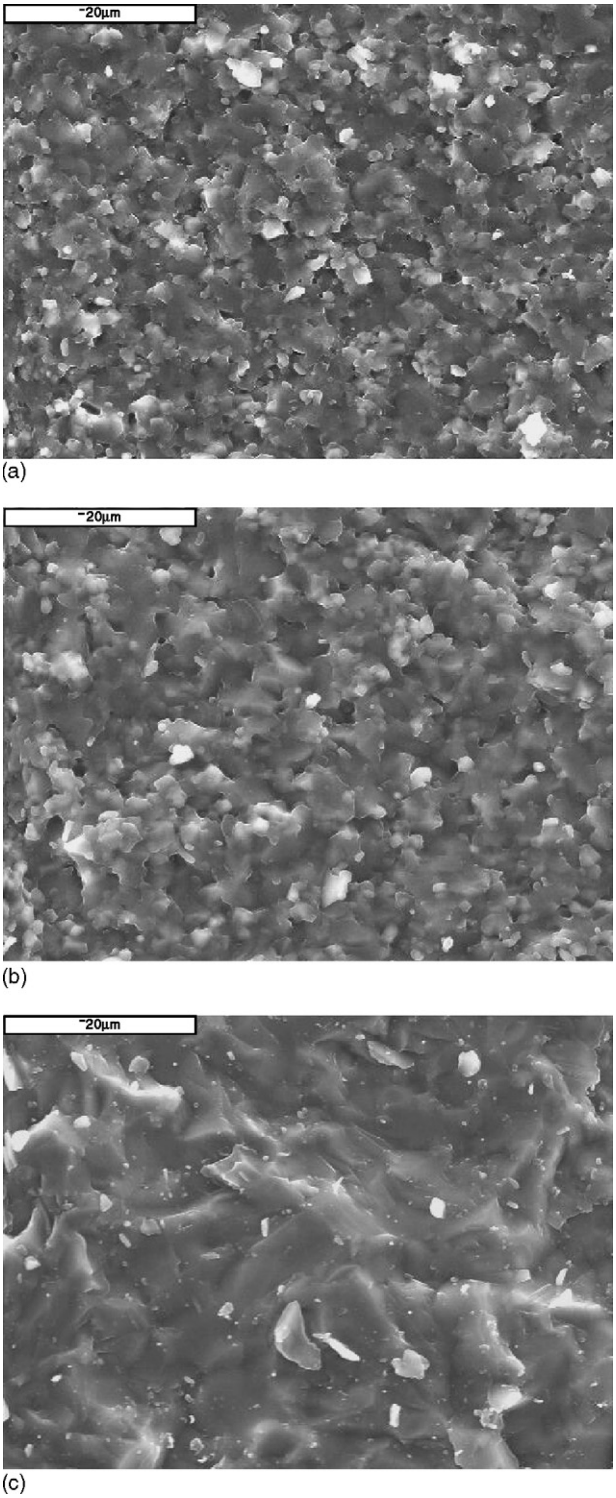

Fig. 7. Microstructure of the samples prepared from mixture of 20% Al and 80% Al_2O_3 and hot-pressed at indicated temperatures: (a) 1750 °C, (b) 1850 °C and (c) 1950 °C.

Relative densities of the hot-pressed samples are shown in Fig. 6. The final materials have relative densities from 96 to 100%. It can be stated that final densities are mainly depended on chemical content of the starting powders and relative weak depended on sintering temperature.

Pictures in Fig. 7 show microstructures of the sample prepared from SHS-derived mixture of 20% Al and 80% Al_2O_3 in the starting composition and then hot-pressed at different temperatures. Uniform microstructure with isometric grains is observed. The average grain size is connected with the sintering temperature and varies from about 2 μm (1750 °C) to 20 μm (1950 °C). Contrary to this observation, the grain size seems to be less dependent on chemical composition of sintered powders.

4. Conclusions

1. The SHS reaction of metallic aluminium and aluminium oxide powder mixtures in nitrogen allows obtaining multi-phase powders with significant content of γ-alon.
2. The powders can be used as active in sintering precursors giving after hot-pressing at temperature above 1750 °C dense (>96%) polycrystalline materials.
3. The sintering process is accompanied by chemical reaction finalizing of γ-alon formation.
4. The near single-phase γ-alon polycrystalline were obtain from the powder synthesized in SHS reaction form the mixture composed of 15% Al–85% Al_2O_3 followed by hot-pressing at 1950 °C for 1 h under 25 MPa in nitrogen.
5. The sintered samples have uniform microstructure with isometric grains which size is controlled by temperature of hot-pressing.

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References

1. McCauley, J. W., A simple model for aluminum oxynitride spinels. *J. Am. Ceram. Soc.*, 1978, **61**, 372–373.
2. Carlone, C. K., Lakin, M. and Shanks, H. R., Optical phonons of aluminum nitride. *J. Appl. Phys.*, 1984, **55**, 4010–4014.
3. Perlin, P., Polian, A. and Suski, T., Raman-scattering studies of aluminum nitride at high pressure. *Phys. Rev.*, 1993, **47**, 2874–2877.
4. Ruiz, E., Alvarez, S. and Alemany, P., Electronic structure and properties of AlN. *Phys. Rev.*, 1994, **49**, 7115–7123.
5. Xidong, W., Fuming, W. and Wenchao, L., Synthesis, microstructure and properties of γ-aluminum oxynitride. *Mater. Sci. Eng.*, 2003, **A342**, 245–250.
6. McCauley, J. W. and Corbin, N. D., Phase relations and reaction sintering of transparent cubic aluminum oxynitride spinel (ALON). *J. Am. Ceram. Soc.*, 1979, **62**, 476–479.

7. Adams, I., AuCoin, T. R. and Wolff, G. A., Luminescence in the system $A1_2O_3$–AlN. *J. Electrochem. Soc.*, 1962, **109**, 1050–1054.
8. Tabary, P. and Servant, C., Thermodynamic reassessment of the AIN–Al_2O_3 system. *Calphad*, 1998, **22**, 179–204.
9. Takebe, H., Kameda, T., Komatsu, M., Komeya, K. and Morinaga, K., Fabrication of translucent sintered aluminum oxynitride spinel [AlON]. *J. Ceram. Soc. Jpn.*, 1989, **97**, 166–173.
10. Fukuyama, H., Nakao, W., Susa, M. and Nagata, K., New synthetic method of forming aluminium oxynitride by plasma arc melting. *J. Am. Ceram. Soc.*, 1999, **82**, 1381–1387.
11. Yamaguchi, G. and Yanagida, H., Study on the reductive spinel—a new spinel formula AlN–Al_2O_3 instead of the previous one $A1_3O_4$. *Bull. Chem. Soc. Jpn.*, 1959, **32**, 1264–1265.
12. Rafaniello, V. and Cutler, I. B., Preparation of sinterable cubic aluminum oxynitride by the carbothermal nitridation of aluminum oxide. *J. Am. Ceram. Soc.*, 1981, **64**, C-128.
13. Ish-Shalom, M., Formation of aluminum oxynitride by carbothermal reduction of aluminium oxide in nitrogen. *J. Mater. Sci. Lett.*, 1982, **1**, 147–149.
14. Zheng, J. and Forslund, B., Carbothermal synthesis of aluminum oxynitride (ALON) powder, influence of starting materials and synthesis parameters. *J. Eur. Ceram. Soc.*, 1995, **15**, 1087–1100.
15. Yawei, L., Nan, L. and Runzhang, Y., Carbothermal reduction synthesis of aluminium oxynitride spinel powders at low temperatures. *J. Mater. Set. Lett.*, 1997, **16**, 185–186.
16. Yawei, L., Nan, L. and Runzhang, Y., The formation and stability of γ-aluminum oxynitride spinel in the carbothermal reduction and reaction sintering processes. *J. Mater. Sci.*, 1997, **32**, 979–982.
17. Bouriannes, R., Hardy, A. and Manson, N., Combustion of an aluminum sphere and identification of the final phase. *C. R. Acad. Sci. Set.*, 1972, **C 274**, 817.
18. Gromov, A., Ilyin, A., Ditts, A. and Vereshchagin, V., Combustion of Al–Al_2O_3 mixtures in air. *J. Eur. Ceram. Soc.*, 2005, **25**, 1575–1579.
19. Kim, Y. W., Park, H. C., Lee, Y. B., Oh, K. D. and Stevens, R., Reaction sintering and microstructural development in the system Al_2O_3–AlN. *J. Eur. Ceram. Soc.*, 2001, **21**, 2383–2391.
20. Kim, I. U. and Richards, V. L., High-temperature electrical conductivity of aluminum oxynitride spinel. *J. Am. Ceram. Soc.*, 1985, **68**, C-120.
21. Corbin, N. D., Aluminium oxynitride spinel. *J. Eur. Ceram. Soc.*, 1989, **5**, 143–154.