Journal of the European Ceramic Society 21 (2001) 2345–2351

www.elsevier.com/locate/jeurceramsoc

Dependence of precursor characteristics on low temperature densification of sol–gel aluminium titanate

U.S. Hareesh[a], A.K. Vasudevan[a], K.G.K. Warrier[a,*], F.J. Berry[b], M. Mortimer[b], F.F. Vetel[b]

[a]Ceramics Division, Regional Research Laboratory (CSIR), Trivandrum-695019, India
[b]Department of Chemistry, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK

Received 9 August 2000; received in revised form 12 December 2000; accepted 2 January 2001

Abstract

Aluminium titanate precursor gels have been prepared by the sol–gel route using monohydroxy aluminium oxide (boehmite) sol and titanium isopropoxide. The influence of calcination temperature of the precursors on phase formation, densification and microstructure development in sol–gel aluminium titanate have been studied. Studies of pre-calcined precursor gels at 600, 800, 1000 and 1200°C show a significant increase in density on raising the calcination temperature from 600 to 1000°C. The treatment at 1000°C favours a phase composition most conducive to low temperature densification of aluminium titanate at 1350°C. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2TiO_5; Calcination; Densification; NMR; Sol–gel processes

1. Introduction

Aluminium titanate, by virtue of its low thermal expansion coefficient, high thermal shock resistance and low thermal conductivity finds potential applications in metallurgy.[1] The characteristics which restrict widespread use of this ceramic is its decomposition to constituent oxides of titania and alumina in the temperature range 900–1200°C, poor mechanical strength and low sinterability.[2] The conventional synthesis of aluminium titanate involves solid state reaction between stoichiometric amounts of alumina and rutile at a temperature $>1450°C$ for complete phase formation. The sintering temperature, on the other hand, is $>1600°C$ and results in enhanced grain growth.[3,4] Earlier attempts have been to use appropriate oxide dopants such as MgO, Fe_2O_3, in order to stabilise the aluminium titanate phase as well as to control the grain growth effects.[5,6] Sol–gel methods have indicated the possibility of decreasing the processing temperatures and hence the possibility of achieving more effective microstructure control.[7,8] Addition of submicron size particles of aluminium titanate has been reported to promote low temperature densification in aluminium titanate precursor gels.[9,10] The effects of addition of low thermal expansion glass, barium salts, ZrO_2 and $ZrSiO_4$ on the sintering behaviour of the alumina-titania system were studied by Nagano et al.[11] and it was observed that such additives gave fine grained microstructures with a small increase in thermal expansion and suppressed the thermal decomposition of aluminium titanate at 1100°C. Incorporation of aluminium titanate in alumina resulted in lower densification temperature.[12] In systems containing alumina and titania, it was found that increasing content of alumina shifted the anatase to rutile transformation to higher temperatures (from 700 to ~1000°C).[13,14] However, not much study has been reported on the effects of thermal decomposition characteristics of sol gel aluminium titanate precursor and associated phase transformations on the densification behaviour of aluminium titanate ceramic under different processing conditions.

Thus, identification of the right precursor conditions and calcination temperature for low temperature dense aluminium titanate formation assumes great significance to obtain a correlation between the final properties of the aluminium titanate and the processing parameters.

---

* Corresponding author. Tel.: +91-471-490674; fax: +91-471-491712.

E-mail address: warrier@csrrltrd.ren.nic.in (K.G.K. Warrier).

PII: S0955-2219(01)00207-2

Such a correlation will enable a tailoring of the parameters to produce the desired microstructure. We therefore report here on the influence of calcination temperature of the precursors on phase formation, densification and microstructure development in aluminium titanate derived from sol gel route.

2. Experimental procedure

The source of alumina used in the preparation of the aluminium titanate precursor gel was boehmite (AlOOH) obtained by the hydrolysis of $Al(NO_3)_3.9H_2O$ (S. D. Fine Chemicals, India).[8] In a typical experiment for preparation of 25 g aluminium titanate, 810.55 g boehmite sol (equivalent to 14.02 g alumina) and 39.05 g titanium isopropoxide (Aldrich Chemicals, USA) were reacted at temperatures less than 5°C. Seed suspension containing 2% by weight of aluminium titanate (average size of seed was ~0.2 μm) was added. The pH of the mixture was adjusted to 5.5 by addition of dilute NH_4OH. The whole reaction system was kept under isothermal conditions at 30°C during the experiment. The gels were dried under humidity conditions of 45°C and 65–75%RH and examined by differential thermal analysis (DTA 50H Shimadzu, Japan).

Dried gel pieces were calcined at 600, 800, 1000 and 1200°C for 2 h each with a heating rate of 3°C/min up to 500°C and 5°C/min above 500°C. They were ground and further ball milled in isopropanol medium for 15 h in a PVC container using alumina grinding media, in order to remove hard agglomerates. The ball milled suspensions were dried and the powders compacted by uniaxial pressing at 50 MPa into circular discs of dia 10 mm and thickness 1.5 mm. using PVA as binder. Alternatively powders were compacted to cylindrical rods of dia 6 mm and height 12 mm for thermomechanical analysis (TMA 50H, Shimadzu, Japan) up to 1400°C. The green pellets were characterized for green density and then sintered at 1300 and 1350°C for 2 h in air. The qualitative phase compositions were obtained from X-ray powder diffraction patterns (Philips PW 1710, The Netherlands). Microstructural examinations (SEM, Jeol JSM 5600 LV, Japan) were performed on sintered samples polished down to 3 μm finish and chemically etched using nitric acid. A Jeol EX- 400 Spectrometer equipped with 5 mm high-speed DOTY probehead, was used to record ^{27}Al MAS NMR (104.05 MHz) spectra for the precursor powders at room temperature. Rotor spinning frequencies were in the region of 9.5 kHz. All experiments employed single pulse excitation with pulse widths less than $\pi/8$, 2 s relaxation delay and typically, 2000 scans. Spectra are presented with exponential line broadening selected to have minimum effect on overall line width. The ^{27}Al chemical shift scale was referenced to external $Al(H_2O)_6{}^{3+}$(aq).

3. Results and discussion

The qualitative phase composition of the powders prepared from gels at pH 5.5 and containing 2 wt.% seeds calcined at 600, 800, 1000 and 1200°C for 2 h is presented in Table 1. Only the anatase phase of titania was observed in the composite gels heated at 600°C. On increasing the temperature to 800°C, γ-alumina and anatase phases were observed. At 1000°C the precursor was a mixture of α-alumina, transitional alumina phases, rutile and anatase phases of titania. The intensity of anatase is almost double that of rutile in the XRD pattern indicating an enrichment by the anatase phase in the mixture. On calcination at 1200°C a mixture of α-alumina and rutile phases were observed. The results show a definite difference in precursor phase constitution on varying the calcination conditions.

Fig. 1 compares the shrinkage patterns of the precursors calcined at different temperatures. The sample calcined at 600 (Fig. 1a) and 800°C (Fig. 1b) indicate a two stage shrinkage profile, first step corresponding to the conversion of transition alumina to α-alumina and the second can be associated with the densification of

Table 1
Phase constitution of the precursor powders calcined at various temperatures

Calcination temperature (°C)	Phases identified by XRD
600	Anatase
800	Anatase and γ-alumina
1000	Anatase and rutile α-Alumina and traces of transition aluminas
1200	α-Alumina and rutile

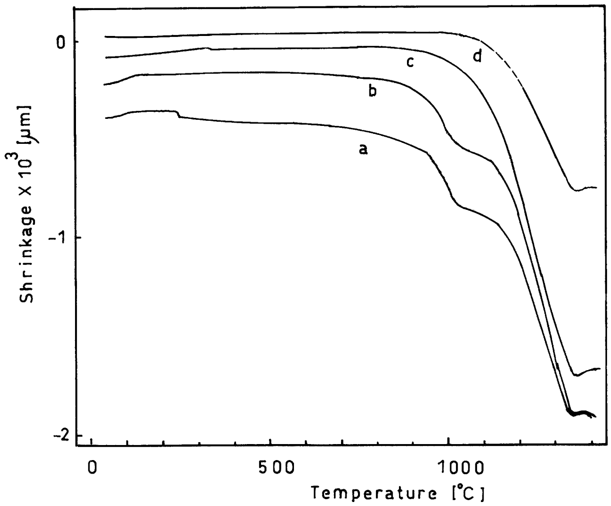


Fig. 1. Thermo mechanical analysis (TMA) patterns of aluminium titanate precursor gels calcined at (a) 600°C, (b) 800°C, (c) 1000°C, (d) 1200°C.

alumina-titania mixture. In contrast, the precursors calcined at 1000°C (Fig. 1c) and 1200°C (Fig. 1d) show single step shrinkage although the former has higher shrinkage but at lower temperature. This indicates an enhanced reaction of the constituents in the precursor calcined at 1000°C and may probably imply that the α-alumina- rutile reactions are enhanced in the presence of transitional aluminas. The aluminium titanate phase formation in all samples is characterized by a small expansion curve at around ~1350°C. This is because aluminium titanate formation from α-alumina and rutile is associated with a 11% molar expansion due to the difference between densities of the constituent oxides and final compound. It can be observed from the shrinkage profiles that in all the samples densification takes place prior to aluminium titanate phase formation.

Table 2
Sintered Density of aluminium titanate prepared from powders calcined at various temperatures

Calcination temperature (°C)	Green density (%TD)	Sintered density (%TD)	
		1300°C	1350°C
600	40	79	80
800	41	80	82
1000	52	96	97
1200	55	91	92

The ball milled precursor powders were dried and compacted with 1 wt.% PVA binder. There is a significant increase in green density values with increase in calcination temperature. The lower calcined samples at 600 and 800°C are extremely fine and the packing efficiency is low compared to powders calcined at higher temperatures of 1000 and 1200°C where there is a broader distribution in particle sizes. Moreover the difference in phases with calcination temperature also contribute to the large variation in green densities. Table 2 shows the dependence of sintered density on calcination temperatures of aluminium titanate precursors on sintering at

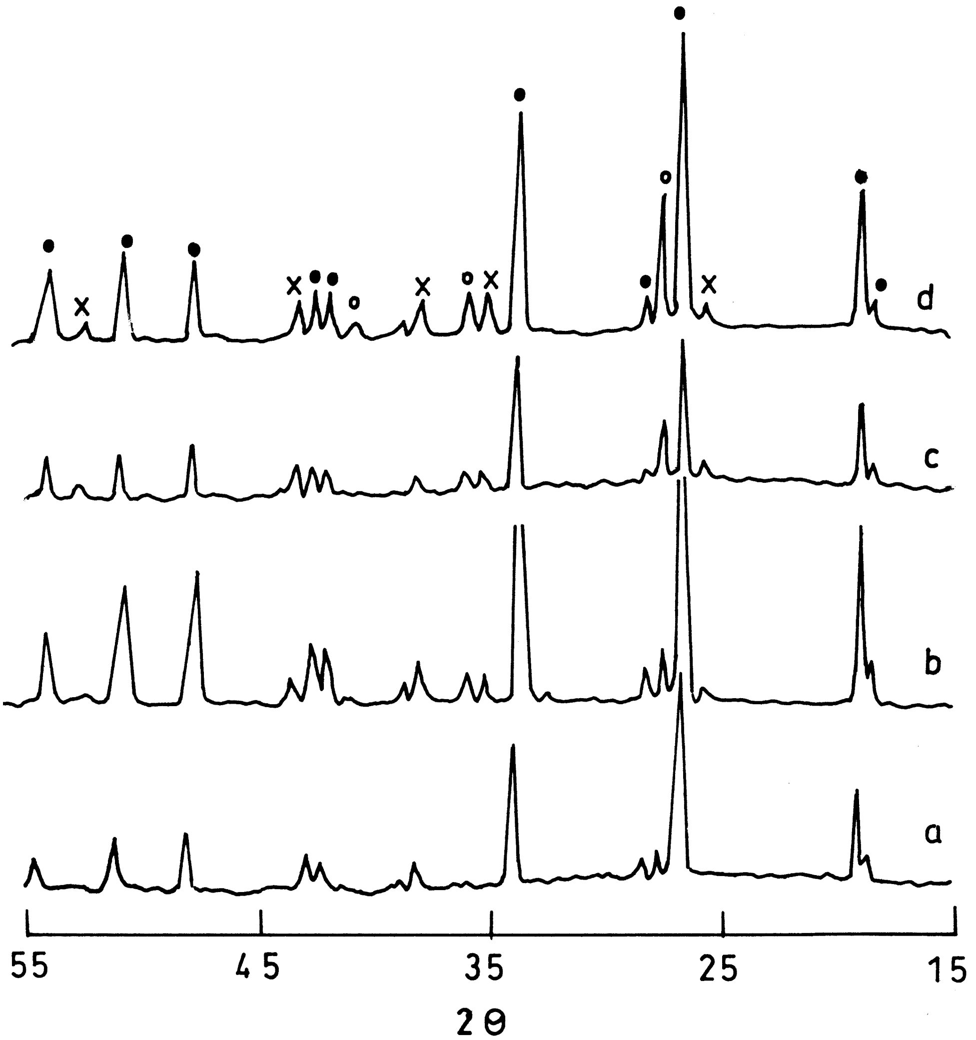


Fig. 2. XRD patterns of aluminium titanate heated at 1300°C obtained from gels calcined at (a) 600°C, (b) 800°C, (c) 1000°C, (d) 1200°C; ● — aluminium titanate, ○ — rutile, × — α-alumina.

1300 and 1350°C. The powders calcined at 1000°C attained maximum densification of 97% TD on sintering at 1350°C. There is a remarkable increase in densification with increase in calcination temperatures from 600 to 1000°C. A lower calcination temperature results in incomplete dehydroxylation and further heating results in weight loss and dimensional changes causing poor densification. Calcination at 1000°C completely dehydroxylates the sample and results in a mixture of anatase and rutile in addition to α-alumina and transition alumina phases. Transition alumina (mixture of δ and θ alumina) and anatase phases are metastable and hence are much more reactive than the stable oxide phases of α-alumina and rutile. Therefore an enhanced sintering and densification is expected for a precursor containing this phase composition. On increasing the calcination temperature to 1200°C, α-alumina and rutile are formed and further densification and reaction takes place at higher temperatures as has been reported previously. XRD patterns of the sintered samples at 1300 and 1350°C are presented in Figs. 2 and 3, respectively. Aluminium titanate is the major phase along with traces of unreacted of α-alumina and rutile. Indeed, the amount of unreacted phases increases with an increase in calcination temperature as is evident from the increase in intensity of the peaks associated with the rutile phase. Hence the sintering temperature was further increased to 1350°C/2 h . Phase analysis of the samples by XRD (Fig. 3) indicated a complete phase formation for samples calcined at lower temperatures of 600 and 800°C (Fig. 3a and b). Traces of unreacted rutile were observed in samples calcined at 1000 and 1200°C.

3.1. ^{27}Al MAS NMR spectra

The ^{27}Al MAS NMR spectra recorded from precursor powders calcined at various temperatures are shown in Fig. 4. The powders calcined at 600 and 800°C give similar spectra and indicate the presence of aluminium in both octahedral AlO_6 and tetrahedral AlO_4 units.[15] The octahedral and tetrahedral resonances are both asymmetric with significant tails to lower frequencies. This behaviour implies a distribution of electric field gradients which could be due to distorted aluminium

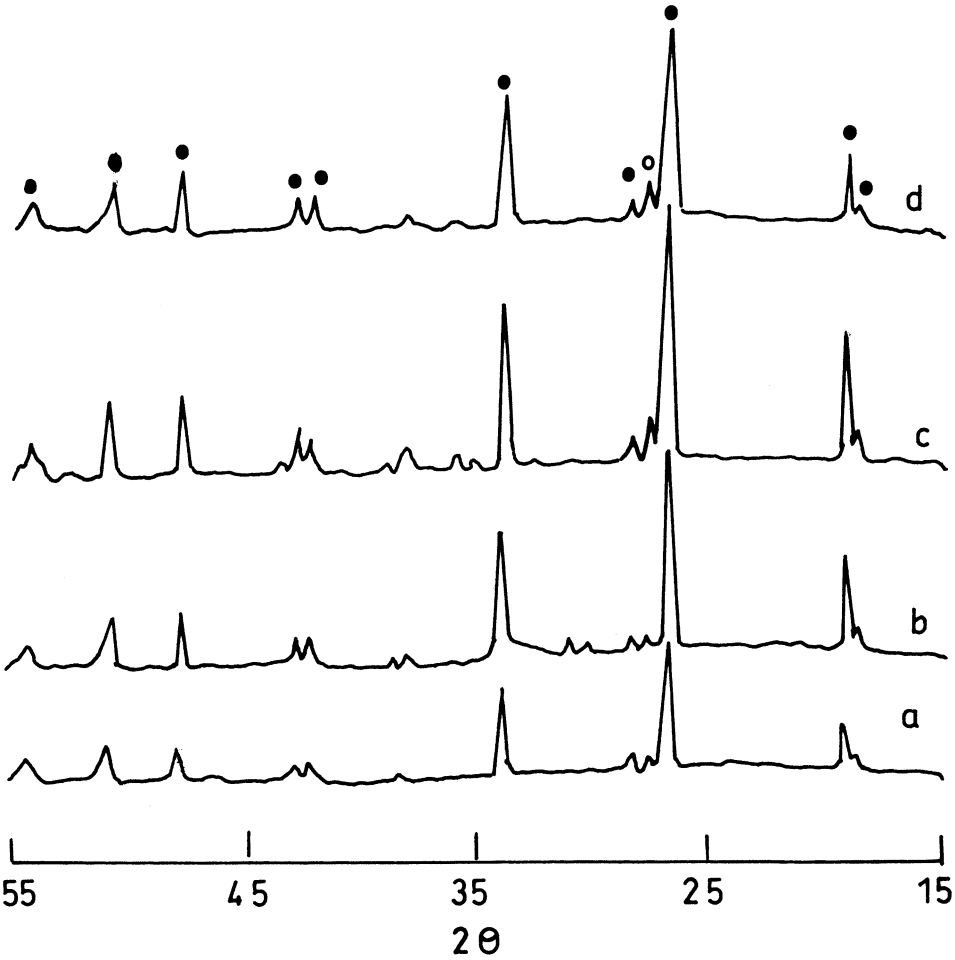


Fig. 3. XRD patterns of aluminium titanate heated at 1350°C obtained from gels calcined at (a) 600°C, (b) 800°C, (c) 1000°C, (d) 1200°C; ● — aluminium titanate, ○ — rutile.

sites with different geometries.[16] Overall the observed spectra are consistent with the presence of transitional alumina phases. On increasing the calcination temperature to 1000°C (Fig. 4c) the aluminium co-ordination becomes completely octahedral and this is also the case for calcination at the higher temperatures of 1200°C (Fig. 4d). For both spectra the peak positions ca.12 ppm, although there will be some influence of second order quadrupole effects, one in the region expected for α-alumina.[15] The ^{27}Al MAS NMR spectrum in Fig. 4e compares well with that reported previously for aluminium titanate.[17] It can be noted that the spread in intensity to

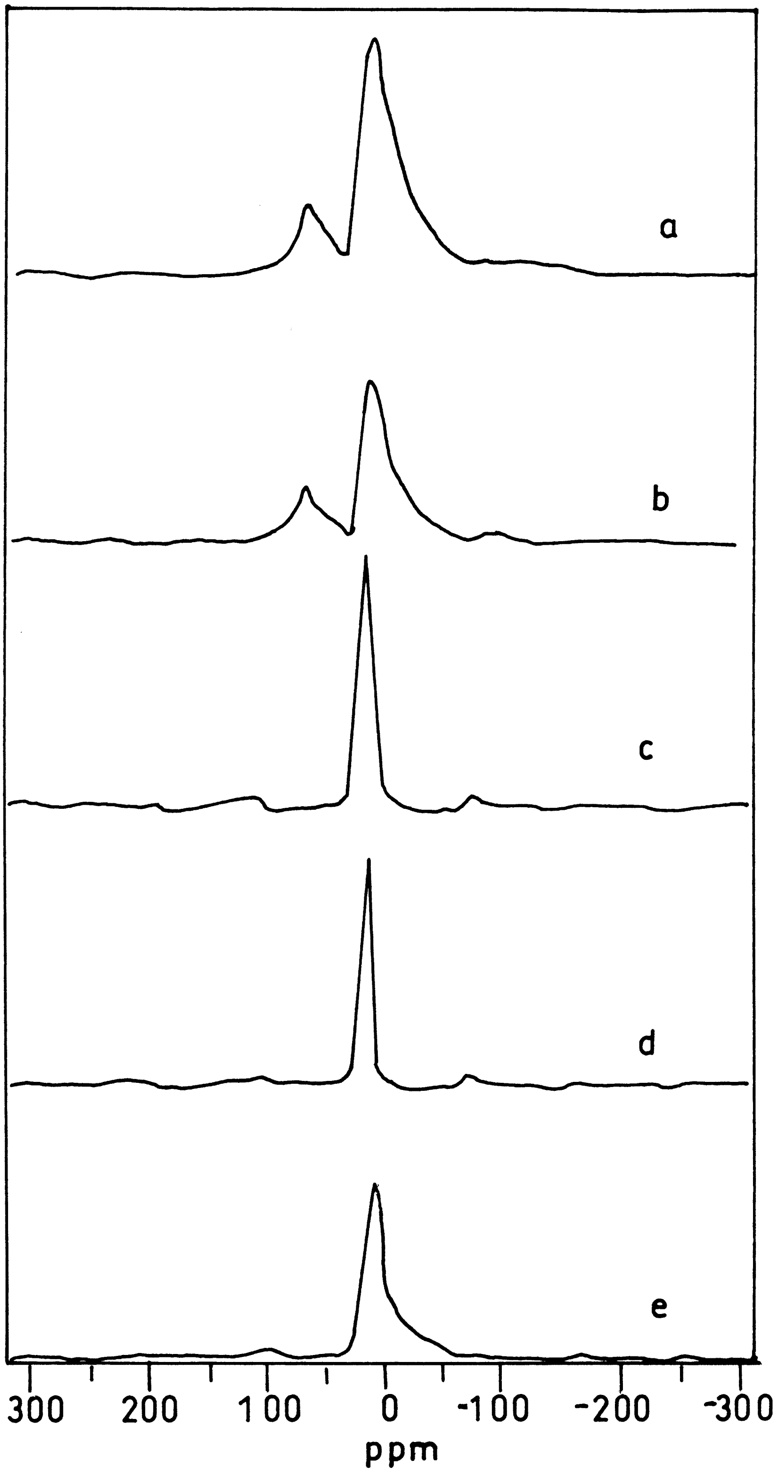
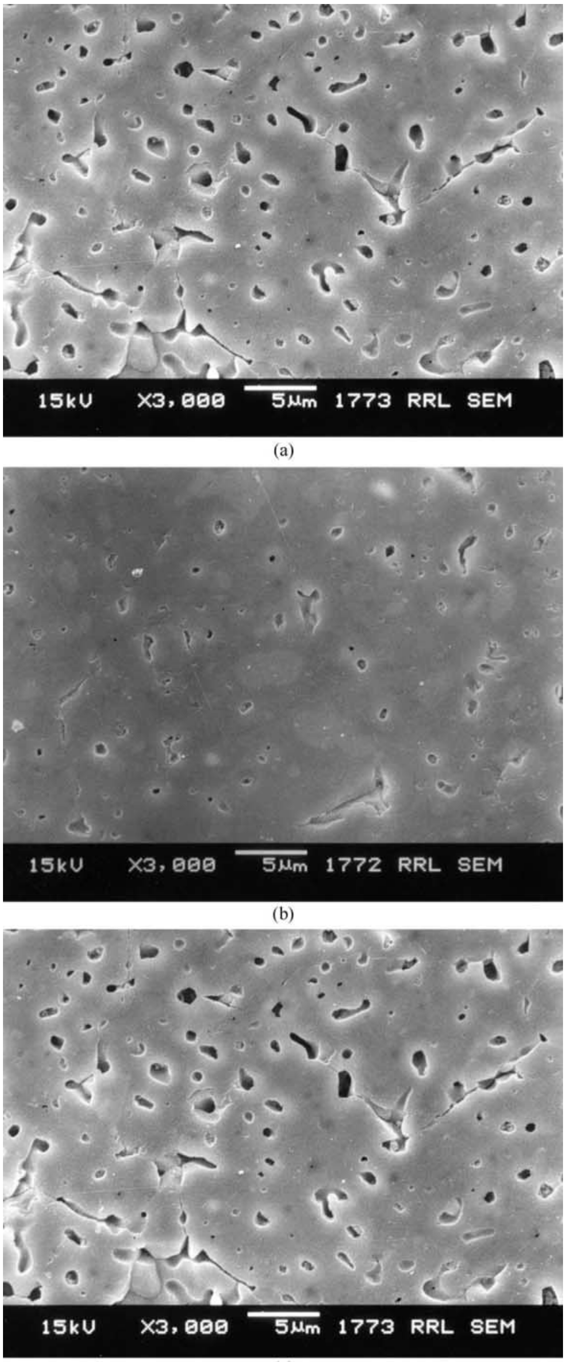


Fig. 4. ^{27}Al MAS NMR spectra recorded at room temperature for precursor powders calcined for 2 h at (a) 600°C, (b) 800°C, (c) 1000°C, (d) 1200°C, (e) 1350°C.



(a)

(b)

(c)

Fig. 5. SEM micrographs of aluminium titanate samples sintered at 1350°C after precalcination at (a) 800°C, (b) 1000°C, (c) 1200°C.

low frequency of the main resonance has been associated with effects due to a distribution in the number of titanium neighbours for a given aluminium site. Alternatively it could be due to crystalline defects giving rise to a spread of electric field gradients. The change to predominantly octahedral co-ordination for aluminium at higher calcination temperatures ($>800°C$)[18] could be a contributing factor in determining the associated sinterabilities as the diffusion rate is known[19] to change with the type of co-ordination. Hence compared to precursors calcined at lower temperatures, the precursor calcined at 1000°C contains aluminium species which confer better sinter qualities and this leads to maximum densification.

Fig. 5 provides the microstructural details of samples calcined at 800, 1000 and 1200°C and sintered at 1350°C/2 h. The SEM micrographs indicate clear distinction between the samples. The 800°C calcined sample is porous(Fig. 5a) and has cracks along the grain boundaries. The sample is poorly densified with significant amount of closed pores within the grains. On the other hand the sample calcined at 1000°C (Fig. 5b) appears to be well sintered with micropores distributed evenly. This is also reflected in the sintered density values (97%TD at 1350°C). Further, when the calcination temperature is 1200°C (Fig. 5c) the microstructure still shows appreciable levels of porosity (sintered density 92% TD).

4. Conclusion

The densification characteristics of the precursor powders obtained after calcination at 600, 800, 1000 and 1200°C vary and low temperature densification is achieved for samples obtained after calcination at 1000°C. The results are associated with the precursor phase constitution, change in aluminium co-ordination sites and reactivity differences of the precursor powders. Preparative conditions based on the sol–gel route have been optimised for obtaining low temperature sinterable phase pure aluminium titanate.

Acknowledgements

Authors U.S.H and A.K.V. acknowledge the Council of Scientific and Industrial Research (CSIR), Government of India for research assistantships.

References

1. Dworak, W. and Fingerle, O., Ceramic materials for engines. *Br. Ceram. Trans. J.*, 1987, **86**, 6170-178.
2. Thomas, H. A. J. and Stevens, R., Aluminium titanate — a literature review, part 1. *Br. Ceram. Trans. J.*, 1989, **88**(4), 144–151.
3. Y. Ohya, Y., Nakagawa, Z. and Hamano, K., Grain boundary microcracking due to thermal expansion anisotropy in aluminium titanate ceramics. *J. Ceram Soc.*, 1987, **70**(8), C184–C186.
4. Freudenberg, B. and Mocellin, A., Aluminium titanate formation by solid state reaction of fine Al_2O_3 and TiO_2 powders. *J. Am. Ceram. Soc.*, 1987, **70**(1), 133–138.
5. Ohya, Y., Hasegawa, M., Nagakawa, Z. and Hamano, K., Effect of some additives on microstructure and mechanical strength of aluminium titanate ceramics. *Report of the Research Laboratory of Engineering Materials, Tokyo Insitute of Technology*, 1987, **12**, 81–91.

6. Kajiwara, M., Sintering and properties of stabilized aluminium titanate. *Br. Ceram. Trans. J.*, 1982, **86**(3), 77–80.
7. Mani, T. V., Pillai, P. K., Damodaran, A. D. and Warrier, K. G. K., Dependence of calcination conditions of boehmite on the alumina particulate characteristics and sinterability. *Mater. Lett.*, 1994, **19**, 237–241.
8. Mani, T. V., Varma, H. K., Warrier, K. G. K. and Damodaran, A. D., Aluminum titanate powder synthesis via thermal decomposition of transparent gels. *J. Am. Ceram. Soc.*, 1991, **74**(6), 1807–1810.
9. Prasadarao, A. V., Selvaraj, U., Komarneni, S., Bhalla, A. S. and Roy, R., Enhanced densifiication by seeding of sol–gel derived alumininum titanate. *J. Am. Ceram. Soc.*, 1992, **75**(6), 1529–1533.
10. Hareesh, U. S., Vasudevan, A. K., Mukundan, P., Warrier, K. G. K. and Damodaran, A. D., Low temperature sintering of seeded aluminum titanate precursor gels. *Mater. Lett.*, 1997, **32**, 203–208.
11. Nagano, M., Nagashima, S., Maeda, H. and Kato, A., Sintering behaviour of Al_2TiO_5 base ceramics and their thermal properties. *Ceramics International*, 1999, **25**, 681–687.
12. Ananthakumar, S. and Warrier, K. G. K., Extrusion characteristics of alumina-aluminium titanate composites prepared by using boehmite as a reactive binder. *J. Eur. Ceram. Soc.*, in press.
13. Rajeshkumar, S., Pillai, S. C., Hareesh, U. S., Mukundan, P. and Warrier, K. G. K., Synthesis of thermally stable, high surface area anatase-alumina mixed oxides. *Mater. Lett.*, 2000, **43**, 286–290.
14. Milosevska, M., Bliznakovsk, B. and Milosevska, R., Sol–gel processing, thermal expansion and some mechanical characteristics of aluminum titanate. *Science of Sintering*, 1993, **25**(1/2), 39–46.
15. Smith, M. E., Application of ^{27}Al NMR techniques to structure determination in solids. *Appl. Magn. Reson.*, 1993, **4**, 1–64.
16. Meinhold, R. H., Slade, R. C. T. and Newman, R. H., High field MAS NMR, with simulations of the effects of disorder on linestape, applied to thermal transformations of alumina hydrates. *Appl. Magn. Reson.*, 1993, **4**, 121–140.
17. Stebbins, J. F., Farnan, I. and Klabunde, U., Aluminium in rutile (TiO_2): characterisation by single-crystal and magic-angle-spinning nuclear magnetic resonance. *J. Am. Ceram. Soc.*, 1989, **72**(II), 2198–2200.
18. Joe, I. H., Vasudevan, A. K., Aruldhas, G., Damodaran, A. D. and Warrier, K. G. K., F. T. I. R. a tool to study high temperature phase transformations in sol gel aluminum titanate. *J. Sol. St. Chem.*, 1997, **131**, 181–184.
19. Zhou, R.-S. and Snyder, R. L., Structures and transformation mechanisms of the eta, gamma and theta transition aluminas. *Acta. Crystallogr. B*, 1991, **47**, 617–630.