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Preparation of tialite (aluminium titanate) via the urea formaldehyde polymeric route

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Abstract

Nano particle size of tialite (aluminium titanate) was prepared through resin formation of 1:2:2 urea, formaldehyde and ethylene glycol, respectively. Up to 1.5 mol Al_2TiO_5 equivalent to (3 mol of $AlCl_3$: 1.5 mol $TiCl_3$) can be substituted in the structure of the resin. The results of FTIR indicate that aluminium occupies tetrahedral and octahedral sites. While the titanium is octahedrally coordinated in the resin structure. Both elements Al^{3+} and Ti^{4+} were homogeneously distributed in the powders prepared as revealed by EDAX. Particle size of the Tialite produced in the fired bodies ranged between 1 and 1.4 μm. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Powders; D. Al_2TiO_5; Synthesis; Chemical preparation

1. Introduction

Tialite (aluminium titanate) caught the attention of researchers working in the field of engineering ceramic materials for its low thermal expansion coefficient and high thermal shock resistance. Usually, it is processed from its constituting oxides mixed in equimolecular proportion and heated above 1300°C.

The product is used as a precursor for further fabrication processes, as reaction sintering gives porous bodies with incomplete formation of tialite [1]. This is overcome either; by using monosized oxide powders [2], or prepared through organo-metallic precursors [3,4] or by additives. Another problem met is the presence of grain boundary micro-cracks. A phenomenon usually met with in highly anisotropic crystalline material and is related to the high thermal expansion anisotropy as reported by Gugel and Schuster [5].

Ohaya et al. [6] in their study demonstrated how the grain size of the titanate bodies was affected by the starting powders. Cracks were conspicuous around grains larger than 3 μm. Also, sintering at a low temperature minimized the number of cracks observed when the grain size was less than 1 μm, about 0.6 μm. Highest strength of 78.9 MPa was obtained when bodies were fired at 1300°C. This value decreases to 60 MPa when fired at 1500°C even to 40 MPa for bodies sintered at 1450°C.

Hennicke and Lingenberg [7] reported that reducing the grain size to minimize the occurrence of grain boundary micro-cracking leads to high stress inside the microstructure that cause the total damage of the fabricated body during cooling.

A critical size between 1 and 2 mm for tialite is recommended to obtain a micro-crack free product as was calculated by Morrow et al. [8] and later given by Holcombe and Coffey [9]. Meanwhile, Ohaya et al. [10] postulated that the critical size varies with sintering temperature, a lower temperature, below 1530°C, shows a larger grain size.

The solid state reactions between the respective oxide powders are the most important method of synthesis for mono- and multi-component systems, utilizing chemically pure processed precursor, as demonstrated by Segal [11].

Formation of tialite proceeds according to the following endothermic reaction:

$$Al_2O_3 + TiO_2 \rightarrow Al_2TiO_5$$

The reaction is accompanied by an increase in molar volume of about 11% [7,12] corresponding to the

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decrease in density of the product. The starting oxides: corundum, rutile or anatase have densities 3.98, 4.25 and 3.89 g/cm^3, respectively, compared with 3.62–3.8 g/cm^3 for the tialite formed [13–15]. Lang et al.[16] were the first to recognize the stability of tialite at low temperatures between 750 and 1300°C. It was related to an eutectoid decomposition taking place in the range 1100–1300°C.

There is still a debate over the mechanism by which decomposition takes place on cooling from synthesis or sintering temperature [7,17,18]. However, it is accepted now, that it is related to nucleation and growth controlled processes of the powder as well as the variables of the process from pressure, sintering temperature and time. Also, residual alumina might act as preferred nucleation sites for decomposition

Segadaes et al. [19] prepared tialite of very fine crystallites that were less susceptible to decomposition by a combustion reaction utilizing urea. The ratio of the reactants was; 2:1:2:5.67 from aluminium nitrate, titanium isopropylate, ammonium nitrate and urea, respectively.

The present work aims at preparing tialite via urea formaldehyde polymeric route. Previous work [20,21] in this field revealed the possible substitution of Al^{3+} and Ti^{3+} in the structure of the resin formed.

Conditions of preparation from concentration of the components, pH, temperature and time of the reaction and characteristics of the powders produced are studied.

2. Materials and methods

Reagent grade chemicals comprising urea (pool BDH 15 Ltd., England), formaldehyde (commercial solution 37–40%), titanium tri-chloride (Merck), aluminium chloride (anhydrous—Aldrich) and ethylene glycol (Aldrich) were utilized for the preparation of tialite (AT).

Aluminium chloride and titanium tri-chloride were added in the stoichiometric proportion to the urea formaldehyde resin (1:2:2 mol from urea:formaldehyde: ethylene glycol, respectively) to obtain 0.5, 1 and 1.5 mol of the compound tialite ($AT_{0.5}$, AT_1 and AT_3) during its formation, Table 1. The optimum amount was 1.5 mol equivalent tialite that gave a clear transparent gel with no signs of precipitation.

Conditions of preparation from pH, concentration, temperature, sequence of addition of the different reactants and time of the reaction were described elsewhere [20]. The colour of the resin developed was deep violet that changed on drying at 120°C first to greenish yellow then to yellowish white. It turns black at 200°C and white powder was obtained at 500°C.

The structure of the resins developed was determined by FTIR-300 E JASCO Fourier Transform Infrared spectrometer. Specimens heat-treated at 120°C were processed in the form of discs using KBr in the ratio 1:200 under a force of 510 kN.

Table 1
Concentration of salt precursors added to the resin

Symbol	Mol of $AlCl_3$	Mol of $TiCl_3$
$AT_{0.5}$	1	0.5
AT_1	2	1
AT_3	3	1.5

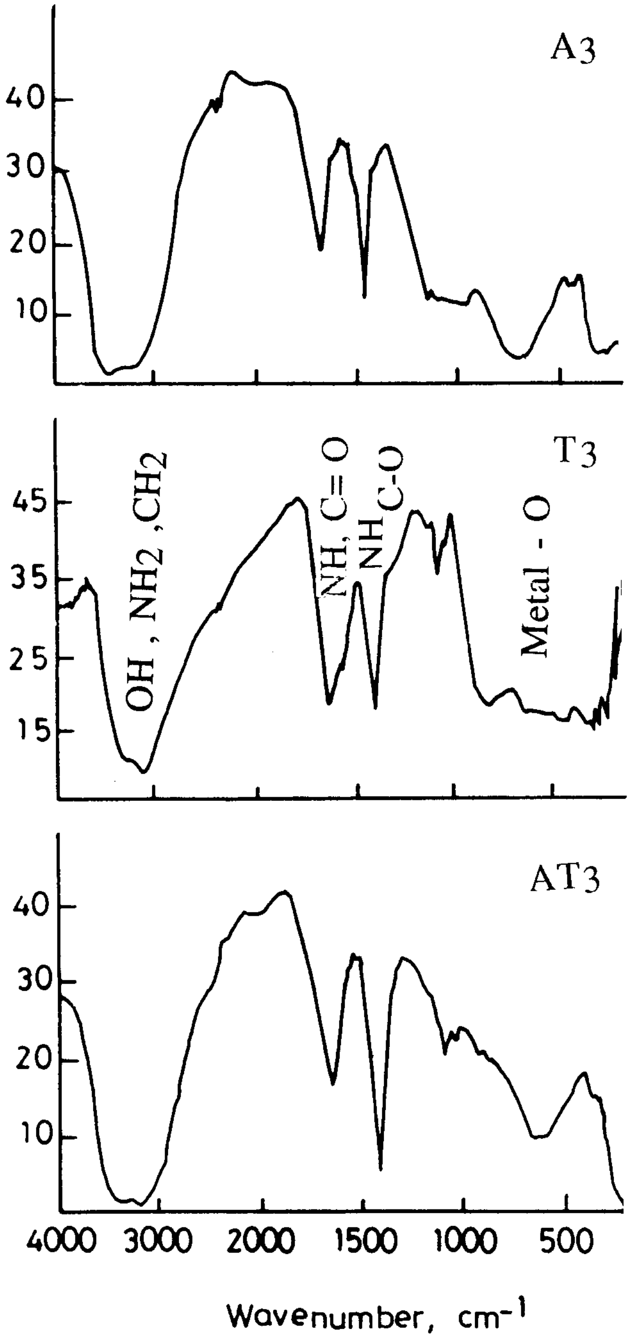


Figure 1. FTIR patterns of resins hosting 3 mol. Concentrations treated at 120°C; A_3; 3 mol $AlCl_3$; T_3: 3 mol. $TiCl_3$; AT_3: 3 mol; $AlCl_3$ + 1.5 mol $TiCl_3$ composite.

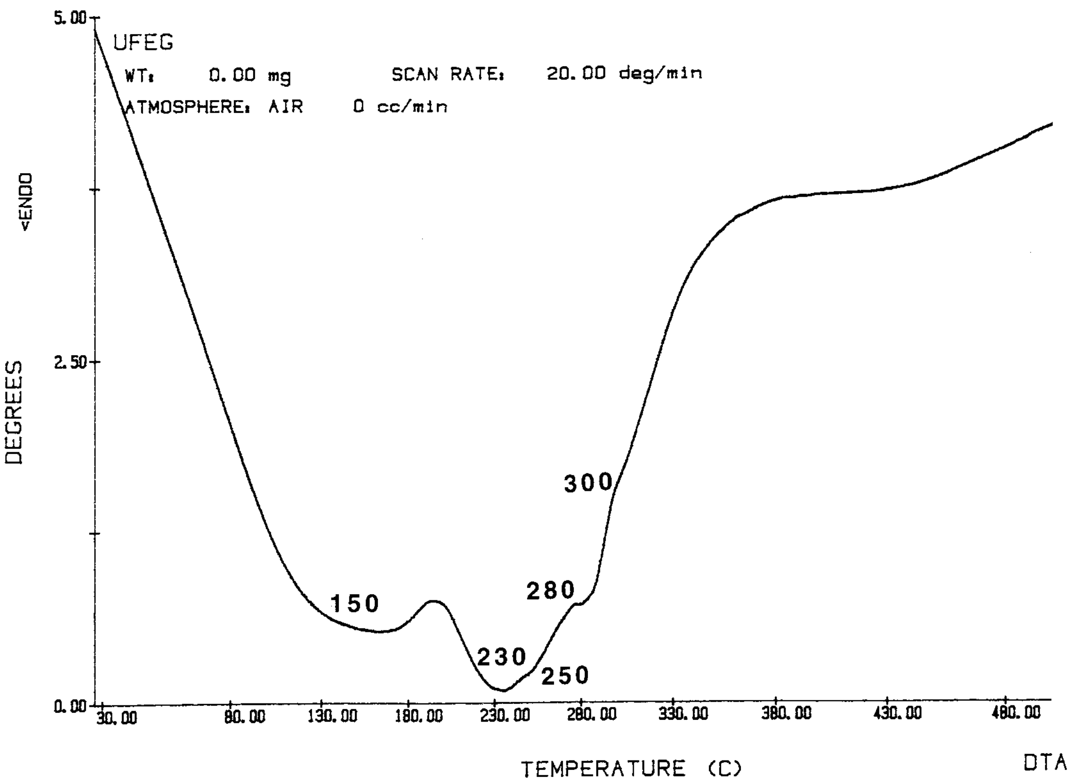


Fig. 2. Thermal analysis DTA of urea formaldehyde-ethylene glycol resin treated at 120°C.

Thermal behaviour was followed by DTA, TG and DTG for the original resin and the resin hosting cations using Perkin–Elmer DTA 1700 system.

Meanwhile, the powders obtained after calcination at 700°C were examined under TEM Jeol type 10005. Pore volume and pore surface area were determined for the same powder samples without compaction by Hg porosimeter Micromerictics type 9810.

Prepared powders from AT_3 were processed in the form of disc specimens under uniaxial pressure of 200 MPa as well as further subjected to cold isostatic pressing (CIP) under 300 and 600 MPa. The processed specimens were fired between 1300 and 1500°C. The formation of aluminium titanate was semi-quantitatively followed from the amount of alumina left unreacted by XRD of the calcined powders.

Selected specimens were subjected to heat treatment at 1100°C for 24 h, then the crystalline phases present were checked by XRD to test the stability of the tialite phase.

Linear thermal changes were followed up to 1500°C by a dilatometer for a specimen processed from AT_3 composite powder calcined at 700°C.

Densification of the specimens was recorded in terms of the relative density. Microstructure was examined under SEM Jeol Type 330A and Cambridge type 590 adapted with EDAX.

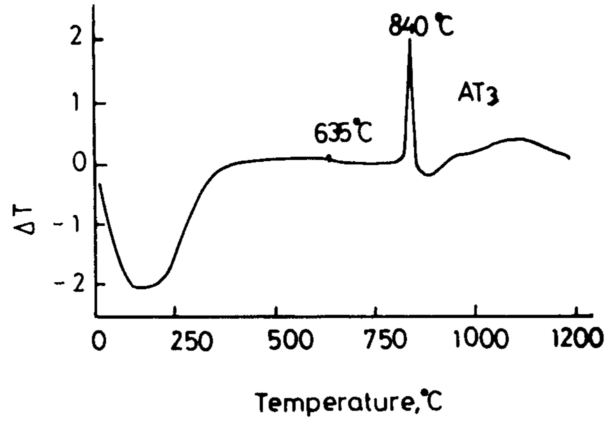


Fig. 3. Thermal analysis DTA of powder calcined at 400°C prepared from resin hosting Al^{3+} and Ti^{3+}.

Table 2
Specific surface area of prepared composite oxide powders

Sample	Calcination temperature (°C)	Specific surface (m^2/g)	Particle (size nm)
AT_1	700	97.43	14.9
AT_3	500	56.57	25.7
AT_3	700	57.92	25.1
AT_3	900	51.73	28.1

3. Results and discussion

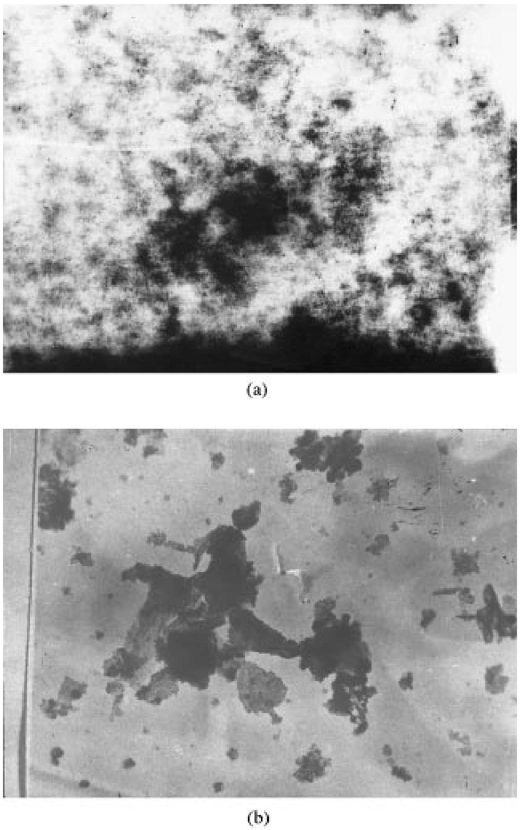
The FTIR spectra of urea formaldehyde resins without and with substituted cations and heat treated at 120°C are shown in Fig. 1. The spectra are clearly differentiated to show the vibration characteristics of NH_2, CH, CH_2, C=O, C–O, C–N. Substitution of either Al^{3+} or Ti^{3+} or both in the hosting resin caused a shift in the major bands. Bands characteristic for Al–O bond appear at 1050, 620, 260, 240, 220 cm^{-1}. A very small band at 840 cm^{-1} is related to Al–N.

Titanium chelated in the hosting resin structure caused a shift in the IR-spectrum. Chelation takes place with CH_2 bands at 1400 and 1078 cm^{-1}. Covalent bond of Ti–O–Ti is evident from the bands 295, 262 and 239 cm^{-1}. Accordingly, on calcination Al^{3+} was tetrahedrally and octahedrally coordinated, while the Ti^{3+} was only octahedrally coordinated.

Introduction of Al^{3+} and Ti^{3+} together to form tialite modified the way of their substitution in the hosting resin than when they were separately added. The covalent bonding of Ti–O–Ti is nearly diminished, a band occurring at 880 cm^{-1}. Metal –O bonding is overwhelming as indicated from the broad bands at 800 to 400 cm^{-1} and 300 to 200 cm^{-1}.

The thermal analysis of the urea formaldehyde resin carried out in air atmosphere, Fig. 2 showed the melting of urea at 150°C as a shoulder. Two endothermic peaks represent dissociation reaction of the resin at 230 and 250°C, respectively. Combustion reaction is represented in DTA by an exothermic peak at 279°C starting just after the second endothermic peak and ends at 300°C. The combustion reaction masks the effect of other reactions taking place during the calcination process of the prepared oxides. Therefore, the powders were scanned after being calcined at 400°C.

DTA of AT_3 powder calcined at 400°C (Fig. 3), shows an endothermic peak occurring at 106°C related to


(a)

(b)

Fig. 4. TEM of composite powder alumina and titania derived from resins hosting different concentrations and calcined at 700°C for 2 h. A: AT_1 mesh work of fine nanometer particles forming a uniform continuous film sheet ×40 000. B: AT_3 pieces of sheet formed have superimposed particles ×20 000.

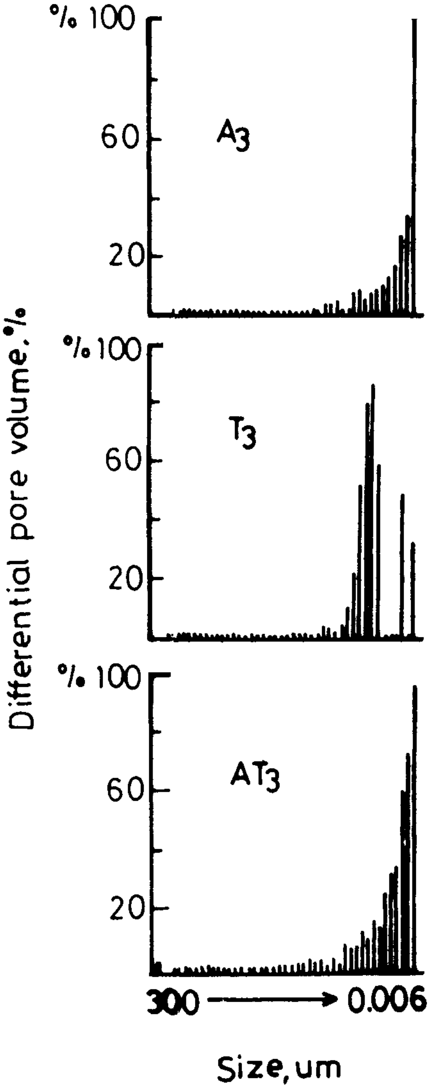


Fig. 5. Differential pore volume of powders prepared from resins hosting 3 mol. Concentration of alumina, titania and alumina + titania composite calcined at 700°C.

adsorbed water. A small exothermic kink at 635°C attributed to the conversion of γ to $-\theta$ alumina, followed by a sharp exothermic peak occurring at 840°C due to the crystallization of rutile. Formation of α-alumina is indicated by the exothermic hump at 1054°C.

Specific surface area values as measured by BET in Table 2 show that AT_1 has a figure approximately double that of AT_3 calcined at the same temperature.

TEM of AT_3 composite powder calcined at 700°C shows a thin film of mesh work of nano-meter particles indicating its very fine nature (Fig. 4).

The pore surface area and pore volume measured for the different powders display the increase in the proportion of micro-capillary and micro-pores with increase in the number of substituted cations in the resin structure. Alumina phases are responsible for the presence of this fraction of pores, as evident from the patterns of the separate components, in Fig. 5.

Results of XRD in Fig. 6 show the presence of titania phases, whether anatase or rutile depending on the temperature of calcination. A mix of both is present in AT_3 calcined at 700°C. While α-alumina phase is identified in both AT_1 and AT_3 in specimens calcined at 1000°C.

SEM of AT composite powder calcined at 700°C shows grains of uniform size and shaped, Fig. 7. The unground crumbles show a glassy appearance as evident in the SEM, Fig. 7. EDAX denotes the stoichiometry of the composite powder AT_1.

From the above results, powders AT_3 calcined at 700°C were selected for body processing. The results of Tialite formation in specimens processed under uniaxial pressure of 200 MPa and fired at different temperatures are shown in Fig. 8. Tialite was first detected at 1300°C. Maximum amount calculated reached 71% and peaks of

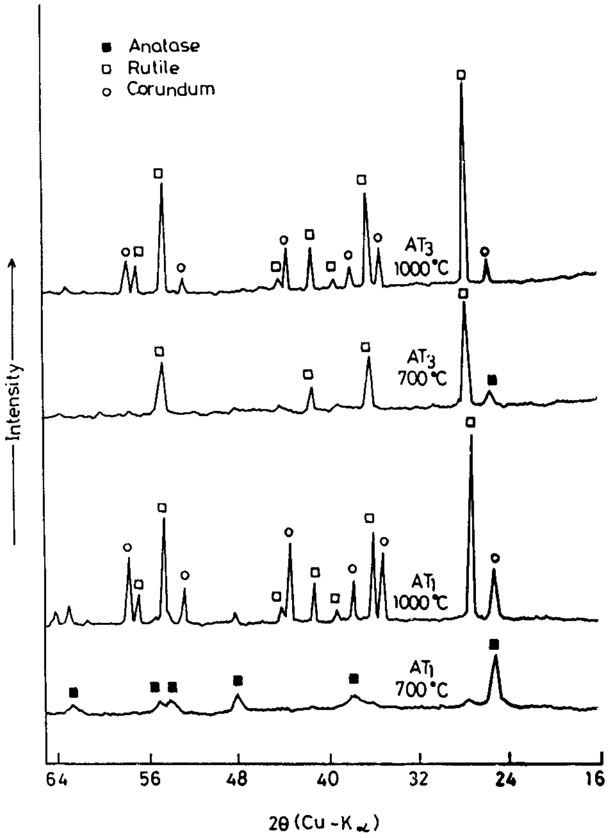
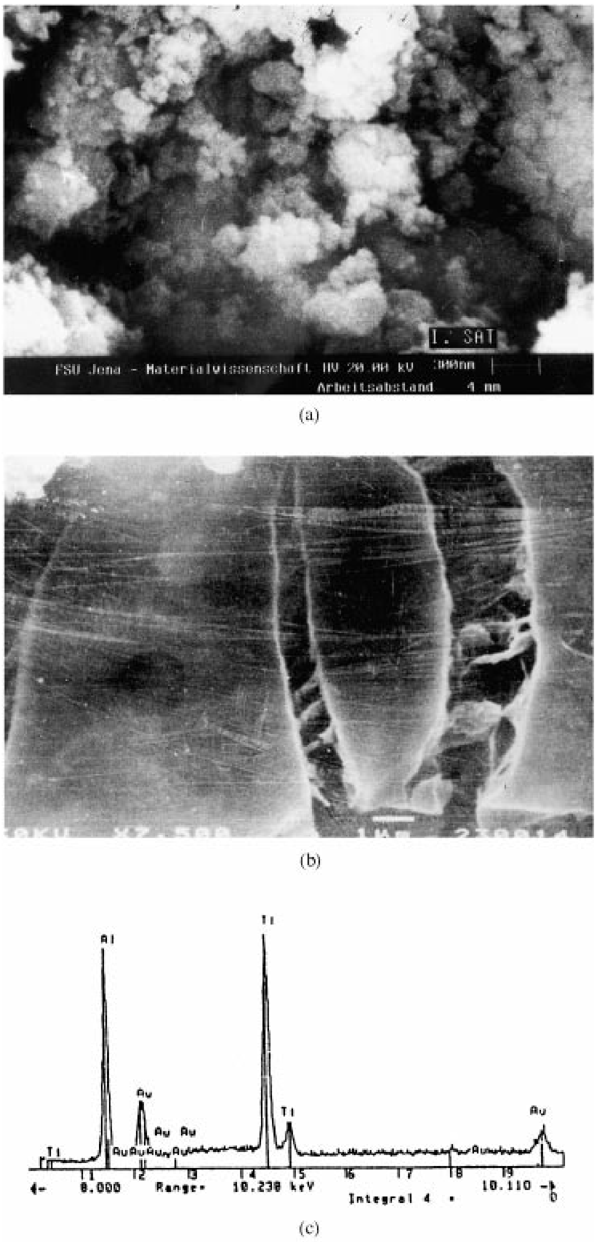


Fig. 6. XRD patterns of alumina–titania composite derived from different concentration hosting resins calcined at 700 and 1000°C.



(a)

(b)

(c)

Fig. 7. SEM of alumina–titania composite powder calcined at different temperatures. A: alumina–titania powder calcined at 700°C fine uniform grains. B: crumble of AT calcined at 1000°C showing the glassy appearance with comb-like structure evident through the crack opening, ×7500. C: EDAX denotes uniform existence of aluminium and titanium in the above SEM.

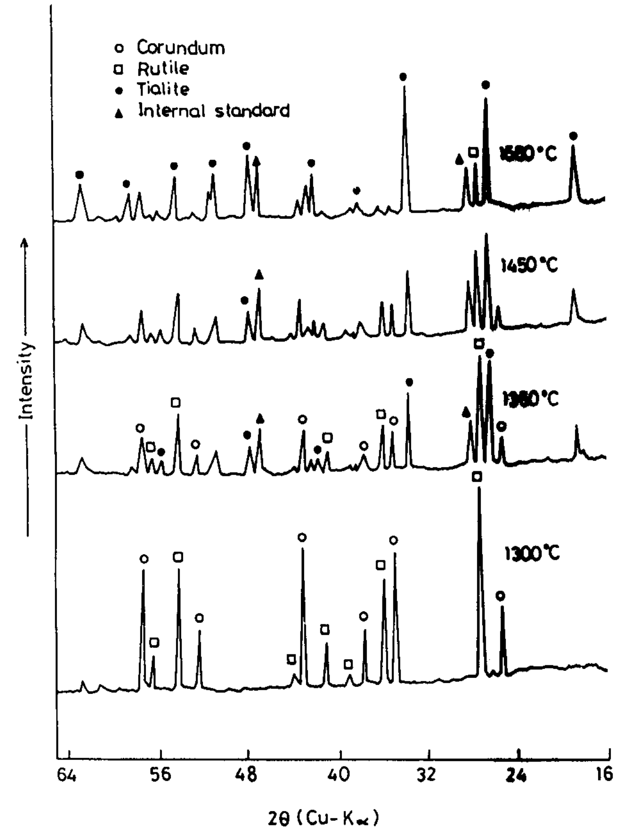


Fig. 8. XRD patterns of uniaxially pressed AT_3 bodies fired at different temperatures.

rutile relics were recorded on firing at 1550°C for 2 h (Fig. 9). These results are in agreement with those reported by Thomas and Stevens [3]

The results of relative density of processed bodies in Table 3 reveal incomplete densification. The thermal linear curve in Fig. 10 showed that densification ended at 1400°C.

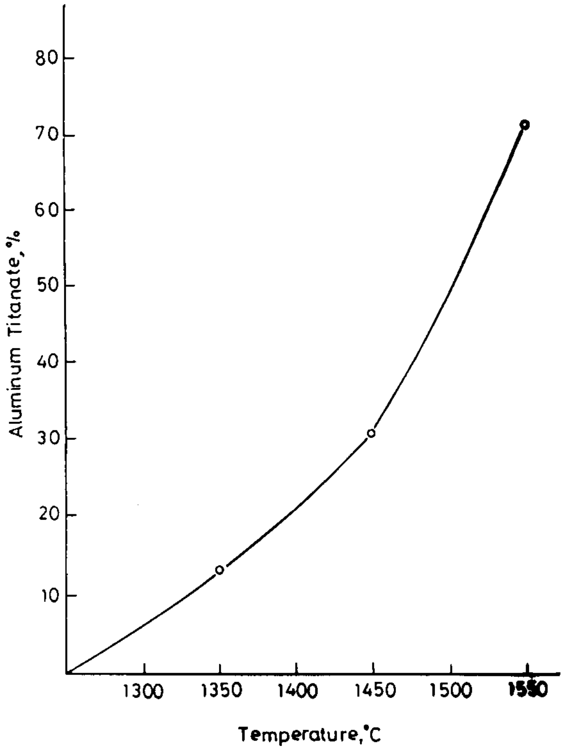


Fig. 9. Following up of tialite formation in AT_3 discs uniaxially pressed under 200 MPa and fired at different temperatures.

Table 3
Densification of processed bodies from AT_3 calcined at 700°C

Firing temperature °C	CIP 300 MPa		CIP600 MPa	
	ρ g/cm^3	R.D.	ρ g/cm^3	R.D.
1300	2.79	73.8	3.31	85.57
1350	–	–	3.18	84.13
1400	2.85	75.4	3.03	80.16
1450	–	–	2.79	74.02
1500	3.01	79.63	–	–

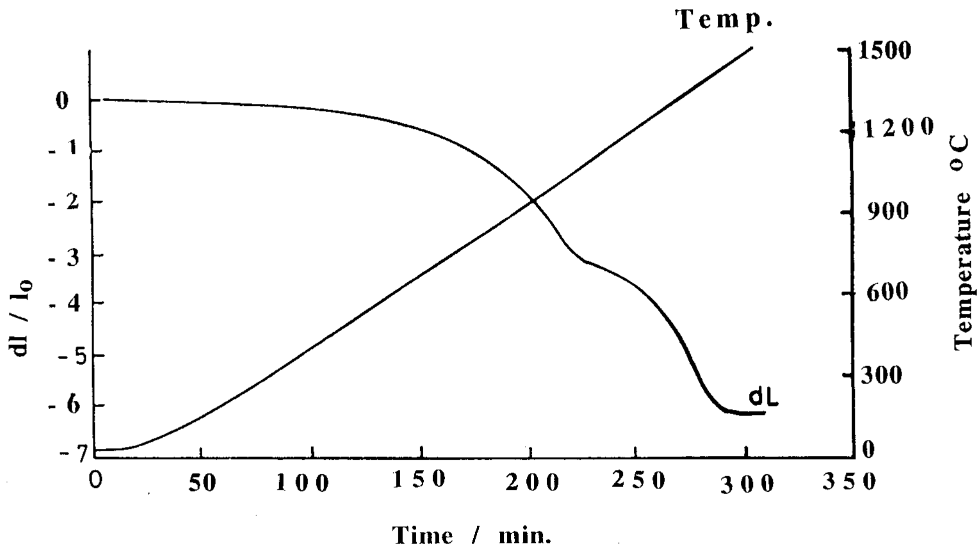


Fig. 10. Linear change of AT_3 bodies isostatically pressed under 300 MPa.

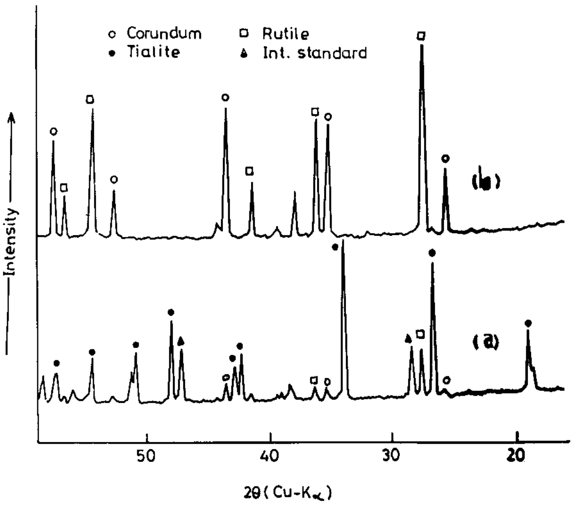


Fig. 11. XRD patterns of uniaxially pressed AT_3 bodies fired at 1550°C for 2 h and subjected to heat treatment at 1100°C for 24 h. A: fired at 1550°C; B: after heat treatment at 1100°C for 24 h.

Selected specimens from the processed bodies that were subjected to heat treatment at 1100°C for 24 h showed complete dissociation of Tialite phase into the starting oxides: rutile and corundum. This is shown in Fig. 11.

SEM (Fig. 12), followed the microstructure of processed bodies fired between 1300 and 1500°C. The specimens are highly porous, and the grains are uniform in size, 1–1.4 μm forming a network of patches and branches of the former resin. Cracks are found along the grain boundaries.

SEM of the specimens fired in the dilatometer up to 1500°C show grains with different dark and gray shades indicating the dissociation of tialite into alumina and titania.

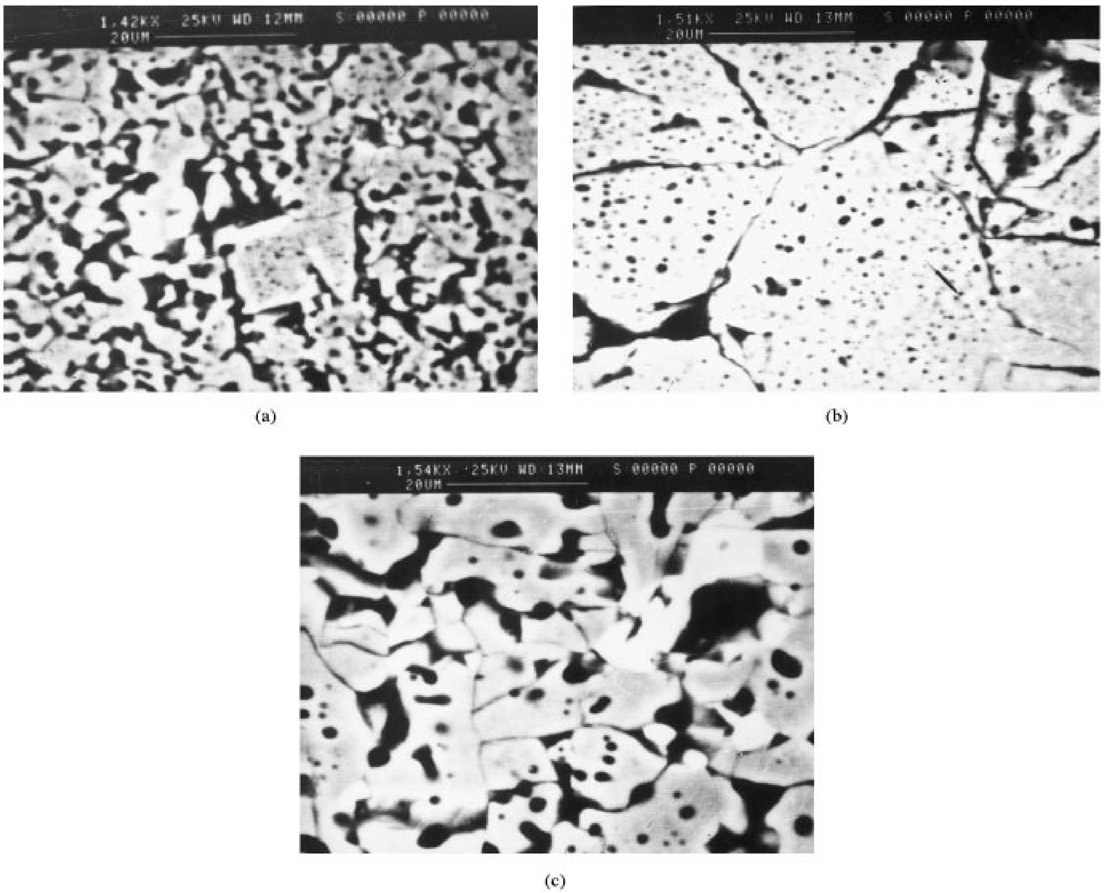
4. Conclusions

It is possible to prepare Tialite in nanometer size starting particles through the urea formaldehyde polymeric route.

Titanium and aluminium were homogeneously distributed in the resin structure. The number of cations substituted in the hosting resins affected the degree of fineness of the powder and type of crystalline phase developed.

Tialite was recorded in specimens fired at 1300°C onwards reaching about 71% at 1550°C.

The grain of tialite is about 3–4 times the size of alumina and titania, but still in the range of critical size less



(a) (b) (c)

Fig. 12. SEM of AT_3 bodies isostatically pressed under 300 MPa and fired at different temperatures. A: 1300°C; B: 1400°C; C: 1500°C.

than 2 μm. Tialite formed totally dissociated on thermal treatment at 1100°C for 24 h.

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