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Densification of alumina produced by urea formaldehyde sol–gel polymeric route

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Abstract

α-Alumina powder was prepared in uniform spherical particles via urea formaldehyde sol–gel polymeric route using aluminium chloride as precursor. Alumina was both tetrahedrally and octahedrally coordinated within the structure of the resin. The α-phase is formed in the powder calcined at 1000°C when the number of Al^{3+} substituted in the resin structure reached 2 moles equivalent oxide. The octahedrally coordinated aluminium form nucleation sites that act as seeds for the formation of α-alumina in powders calcined at 700°C. Bodies processed by cold isostatic press (CIP) under 300 and 600 Mpa from this powder show densification approaching to about 94% total density TD when fired at 1550°C . Grain growth was observed in microstructure of bodies fired at 1700°C and densification was lowered to 90.9% TD.

1. Introduction

Performance of ceramic components is dependent on the microstructure developed which in its turn is a reflection of the physical and chemical characteristic of the starting powders and their behaviour during processing.

Surface activity of ultrafine powders is one of the major driving forces in the densification process during solid state sintering. Improved sinterability is attained by using powders with controlled morphology, size and size distribution. These requirements are achieved by using synthesized powders. The common precursors include either alkoxides or inorganic salts.

Yoldas [1–5] dealt with the preparation of alumina sols from alkoxides and adjusted the conditions of preparation. Al-isopropoxide and Al-*sec*-butoxide were used as precursors. Hydrolysis and peptization reactions of the alkoxide governed the particle size achieved.

In a review, Blendell et al. [6] they demonstrated how sub-micron, monosized particles could be formed by heating Al-chloride and perchloride solutions. Boehmite is the alumina phase obtained. Particles are ellipsoid in shape with an average surface area 200 m^2/g, but contain a large amount of chlorine that needed to be leached by soaking in a basic solution.

Johnson [7] recorded that alumina powder can be made by spray drying with an average particle size 10 μm. However, smaller sizes around 1 μm could be obtained by aerosol technique.

The amphoteric nature of aluminium ion in aqueous solution is well known. Hydrated aluminium hydroxide is precipitated only in a solution with a narrow pH range between 5.4 and 7.

Cornilsen and Reed [8] used urea as an agent to produce aluminium hydroxide precipitate that is easier to filter than that obtained by rapid addition of a base. Precipitation depends on the hydrolysis of urea and the gradual rise in pH which can precipitate a basic Al-salt on heating at 80–90°C. In comparison with urea, formamide is a better precipitating agent. It does not yield a gas allowing better control of contamination. It may be better than urea for producing monosized particles because of the high initial rate of pH change as reported by Blendell et al. [6]. In general, the smaller size is assured by the lower aluminium concentration and the shorter heating time.

Djurcic et al. [9] used glucose and urea 1:2 in the molar ratio to produce fine alumina powder. Thus the organic complex was made by melting at 150°C.

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The polymerization reaction taking place between urea and formaldehyde to form the respective resin was utilized by Ibrahim et al. [10] to prepare ultra-fine alumina powders. Aluminium chloride or aluminium sec-butoxide precursors were introduced during resin formation. The powder of α-alumina obtained after calcination at 1000°C was formed of spherical equigranular particles with size about 8 nm.

The present work aims at preparing alumina via urea formaldehyde polymeric route using aluminium chloride as precursor and studying the densification and microstructure of the processed bodies.

2. Materials and methods

Chemically pure reagent grades were used as precursor materials including; urea and formaldehyde; aluminium chloride; ethylene glycol. The molar ratio 1:2:2 of urea : formaldehyde : ethylene glycol to (1, 2, 3 or 4 moles of aluminium chloride to give samples A_1, A_2, A_3 and A_4, respectively) were prepared to optimize the number of molecules of aluminium that can enter the structure of the resin during polymerization reaction. Ethylene glycol was used partly to terminate the reaction. The conditions of the reaction; temperature, pH, time and sequence of addition of the different components were optimized elsewhere [10]. A flow chart of the method used is shown in Fig. 1.

The gels produced were slowly dried and then calcined in a stream of air up to 700°C until complete charring occurred and further heated up to 1000°C. Product is in the form of clusters, that is ground to give the respective powders. Morphology of the grains was studied under TEM Jeol type 1005 for dispersed powders.

Clusters were examined under SEM JSM-T-330A and Cambridge type 590 with EDAX from Tracor. Thermal analysis comprising DTA, TG and DTG for samples A_1 and A_3 were carried out using a Perkin–Elmer DTA 1700 system. Pore size volume and pore surface area in powders calcined at 700°C and 1000°C were determined using Hg-porosimeter Type 9810. Phases developed during calcination were determined by XRD using a Philips apparatus type 1700 and copper radiation with a Ni filter. Prepared powders calcined at 700°C were processed under uniaxial press (200 MPa) and under isostatic press (300 and 600 MPa). Cylindrical specimens with the following dimensions diameter 8 mm and thickness 5 mm were fired between 1550 and 1700°C with 1 h soaking period. Densification of the fired specimens was followed from the results of bulk density and relative density. Selected specimens were polished with three grades of diamond pastes 7, 2, 0.5 μm then thermally etched at 150°C below the respective firing temperature and examined under the SEM.

3. Results and discussion

The DTA curves in Fig. 2 show the thermal behaviour of the resin hosting different concentration of Al^{3+} cations. The degree of sharpness of the peak and its position varied accordingly. The endothermic peaks are related to the melt and the dissociation of the resin and occur at 131 and 325°C or 142 and 311°C for low and high Al^{3+} cation concentrations, respectively.

TG shows the accompanying loss in weight. The DTG curves indicate that the main loss in weight takes place below 400°C in a combustion reaction. White powder is obtained earlier in the low concentration resin. DTA of powder calcined at 400°C shows endothermic peak at 319°C attributed to the transformation of Boehmite into γ-alumina. Two exothermic peaks characteristic of alumina phase transformation; γ to θ then to α occurring at 839 and 1092°C, respectively Fig. 3.

Alumina powders produced are very fine in nature, Fig. 4. The measured particle size from TEM coincides with the value calculated from specific surface area results 15.8 and 16.7 nm for sample A_3, respectively. While, α-alumina formed at 1000°C has a particle size 1.36 μm as measured from XRD broadening technique.

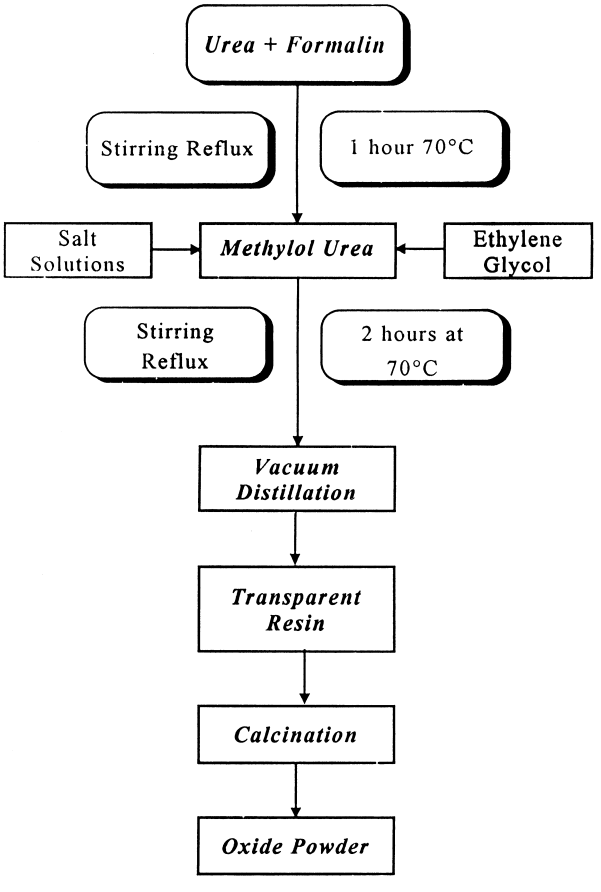

Fig. 1. Flow chart of the current method.

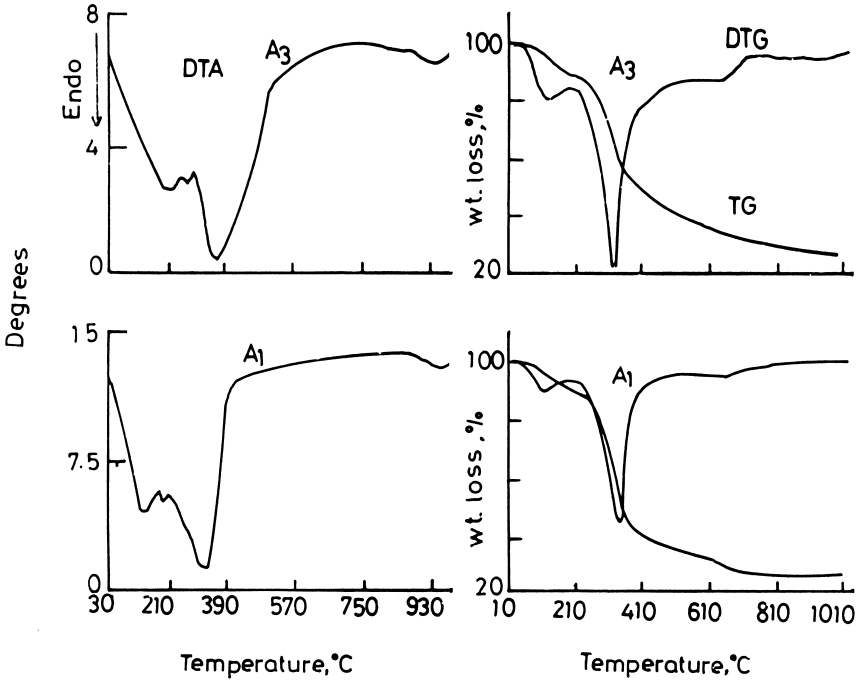

Fig. 2. Thermal analysis DTA, TG and DTG of resins hosting different concentrations of Al^{3+} (A_1 and A_3 low and high) treated at 120°C.

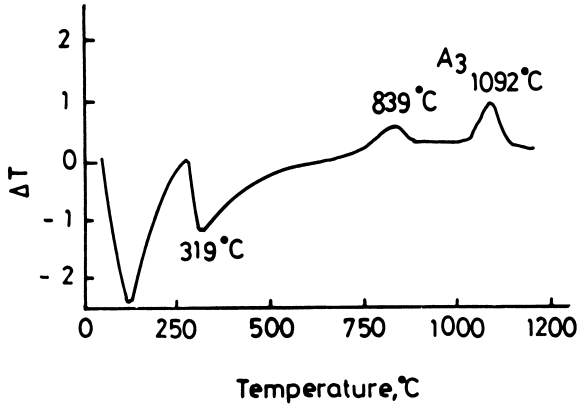

Fig. 3. Thermal analysis DTA of powder A_3 calcined at 400°C prepared from resin hosting Al^{3+}.

According to Messing and Kumagai [11] synthesis of dense discrete nano-size particles between 10 and 200 nm, requires control over nucleation, growth and coagulation processes. Sugimotto [12] postulated that the accumulation of ions on a nucleus will result in euhedral particle formation. Meanwhile, spherical particles are attributed to accumulation of polymeric species onto the nuclei. Matijevic [13] has recorded how the effect of change in solution chemistry; as concentration, pH and temperature can alter the morphology of the particles, significantly.

TEM and SEM of alumina crumbles and powders derived from resins hosting cations of different concentrations calcined at 700°C are shown in Figs. 4 and 5 consisted of very fine equigranular more or less spherical particles less than 1 μm preserving the

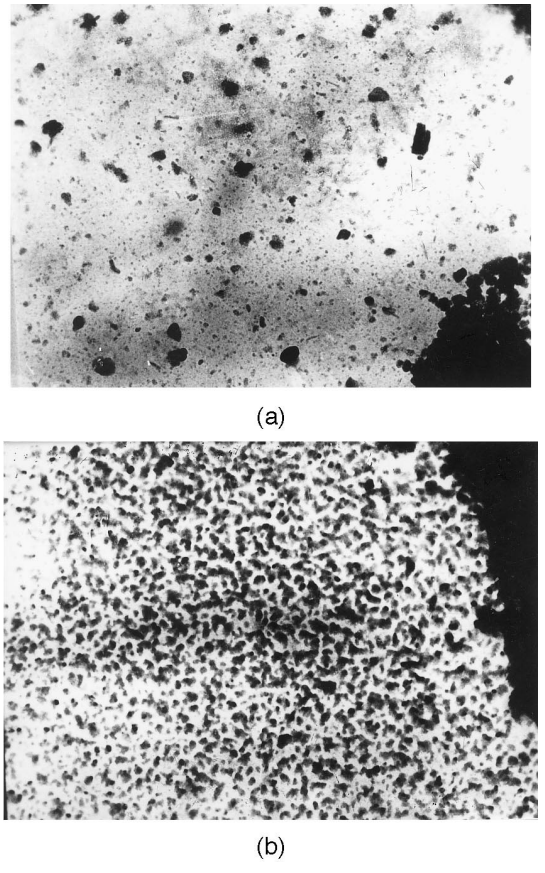

Fig. 4. TEM of alumina powder derived from low and high concentration resins hosting cations, calcined at 700°C. (a) A1 segment of the chains and very fine grains ×:125000; (b) A_4 polymer structure preserved branches and rings ×:63000.

former structure of the resin. These findings indicate that the polymeric nature of the resin played a role in the formation of spherical particles and in providing the nuclei of the various cations coordinated in the structure.

These results were not achieved by authors working in the field of synthesizing ceramic precursors via chemical preparations. Thus, the utilization of alkoxide [1], which is the commonest precursor in sol–gel processing, the powders obtained are in the form of spherical agglomerates, the size of which is dependent on the conditions of preparation. In spray pyrolysis technique solid or hollow spherical particles less than 20 nm size were obtained on the application of ultrasonic dispersion during processing.

The results of pore surface area and pore volume of powders calcined at 700 and 1000°C, Fig. 6, show a decrease in the proportion of macropores with increase in the number of cations substituted in the former resin structure. The fine pore fraction less than 0.006 μm is overwhelming and is responsible for the pore surface area values. Increasing the umber of cations in the hosting resin gives rise to enrichment of micropores in the prepared alumina powders.

XRD patterns of the powders calcined at different temperatures showed amorphous nature up to 700°C Fig. 7. Whereas very small peaks of γ; and θ together with α-alumina are detected in the powder calcined at 1000°C. These results indicate the same sequence of crystallization of powder obtained in other synthesizing chemical routes described by Iller [14].

This confirms the view of overwhelming octahedral coordination of Al^{3+} in the resin structure over the tetrahedral ones [15]. The octahedral coordinated Al^{3+} readily form nuclei for the early crystallization of α-phase. This means that in the applied method of preparation γ and θ phases are the only intermediate transition forms that crystallized and transformed to α-alumina at

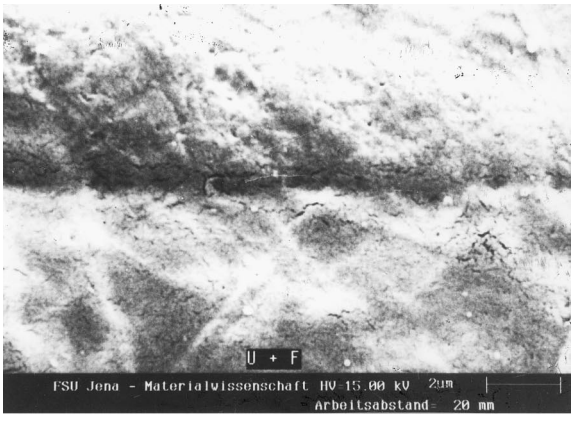

Fig. 5. SEM of prepared resin and calcined powder. (a) Sheet of urea formaldehyde resin free from cations treated at 150°C; (b) A_3 powders calcined at 700°C lace like microstructure with homogeneous distribution of micropores; (c) A_3 unground powders calcined at 700°C, preserving original structure with glassy appearance and cracks.

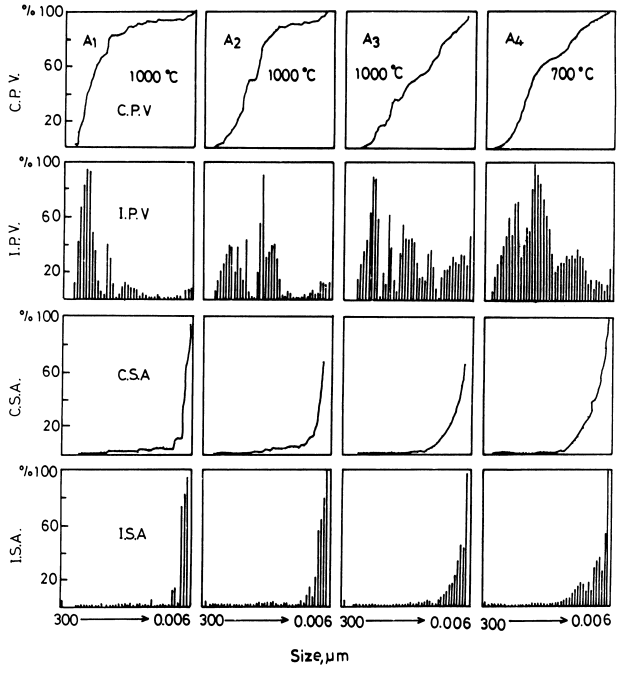

Fig. 6. Pore size distribution in alumina derived from different concentration hosting resins calcined at 700 and 1000°C. C.P.V: cumulative pore volume; I.P.V: incremental pore volume; C.S.A: cumulative pore surface area; I.S.A: incremental pore surface area.

1000°C i.e. 200°C earlier than that mentioned by Iller; 1200°C. Also, with the increase in the number of Al^{3+} cations substituted in the hosting resin structure, the opportunity for α-phase to form increases. This is demonstrated by the results of XRD of sample A_3 where α-alumina is the sole phase at 1000°C.

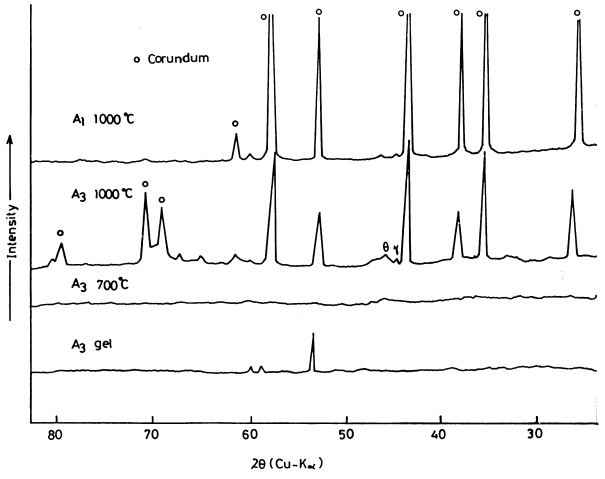

Fig. 7. XRD patterns of alumina powders derived from hosting resins calcined at different temperatures.

Isostatically processed bodies under 300 MPa from A_3 and A_4 specimens fired at 1550°C show 93 and 91% of TD, respectively. Meanwhile, bodies of A_3 processed under 600 MPa showed better densification when fired at 1650°C reaching 93.45% of TD then decreased to 90.93% with rise of temperature of firing to 1700°C. Whereas, bodies processed from A_4 powders calcined at different temperatures, pressed under 600 MPa were poorly

Table 1
Densification properties of processed bodies

No. of mix	Calcination temperature (°C)	Firing temperature (°C)	300 MPa		600 MPa	
			D	RD %	D	RD%
A_3	700	1450	3.52	88	–	–
	700	1550	3.72	93	3.04	76.57
	700	1600	3.37	84.88	–	–
	700	1650	–	–	3.71	93.45
	700	1700	–	–	3.61	90.93
A_4	700	1450	3.41	85.89	xxx	xxx
	700	1550	3.64	91.69	2.74	69.02
	800	1600	–	–	3.11	78.34
	800	1650	–	–	3.54	89.17
	800	1700	–	–	3.51	88.41

xxx, Damaged; D: bulk density; RD: relative density.

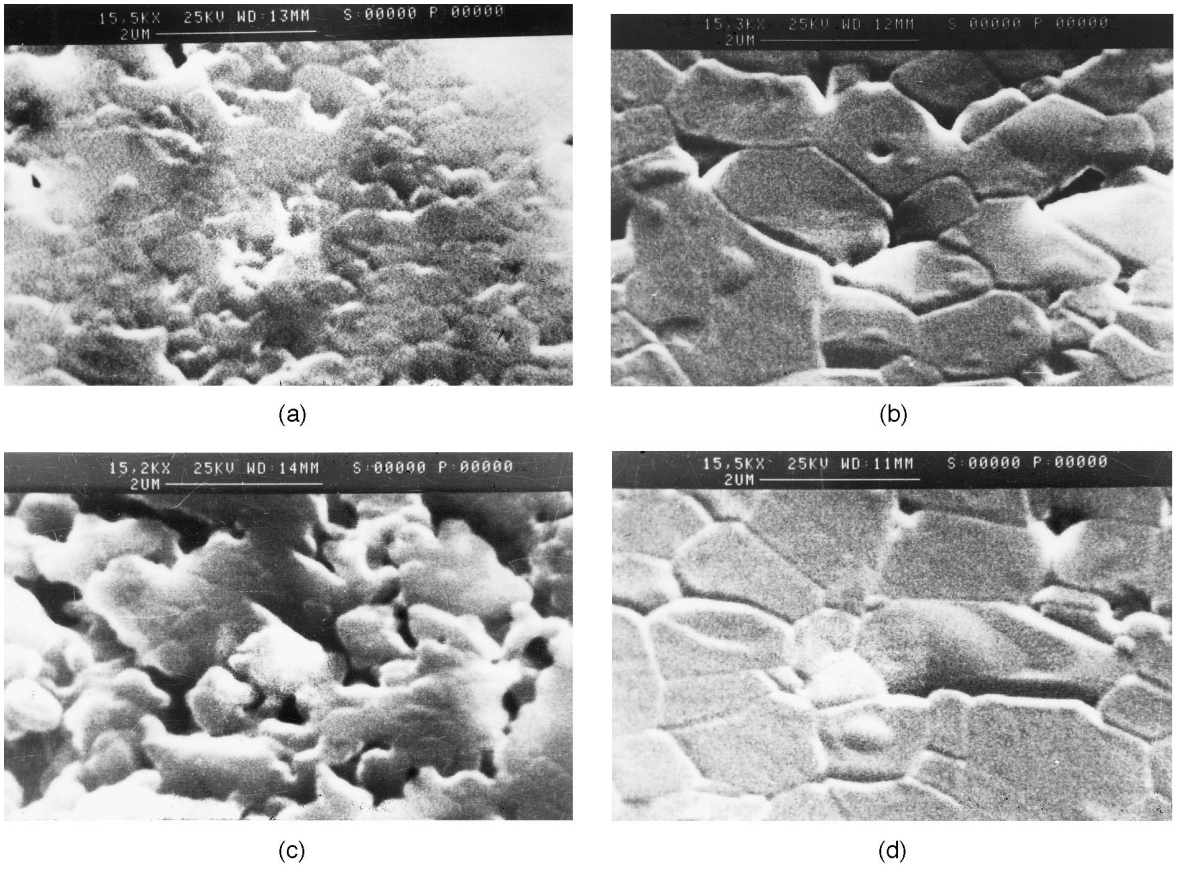

Fig. 8. SEM of alumina bodies isostatically pressed under 300 Mpa,fired at different temperatures, fine equigranular grains sintered in patches. (a) A_3 bodies fired at 1450°C; (b) A_3 bodies fired at 1550°C; (c) A_4 bodies fired at 1450°C; (d) A_4 bodies fired at 1550°C.

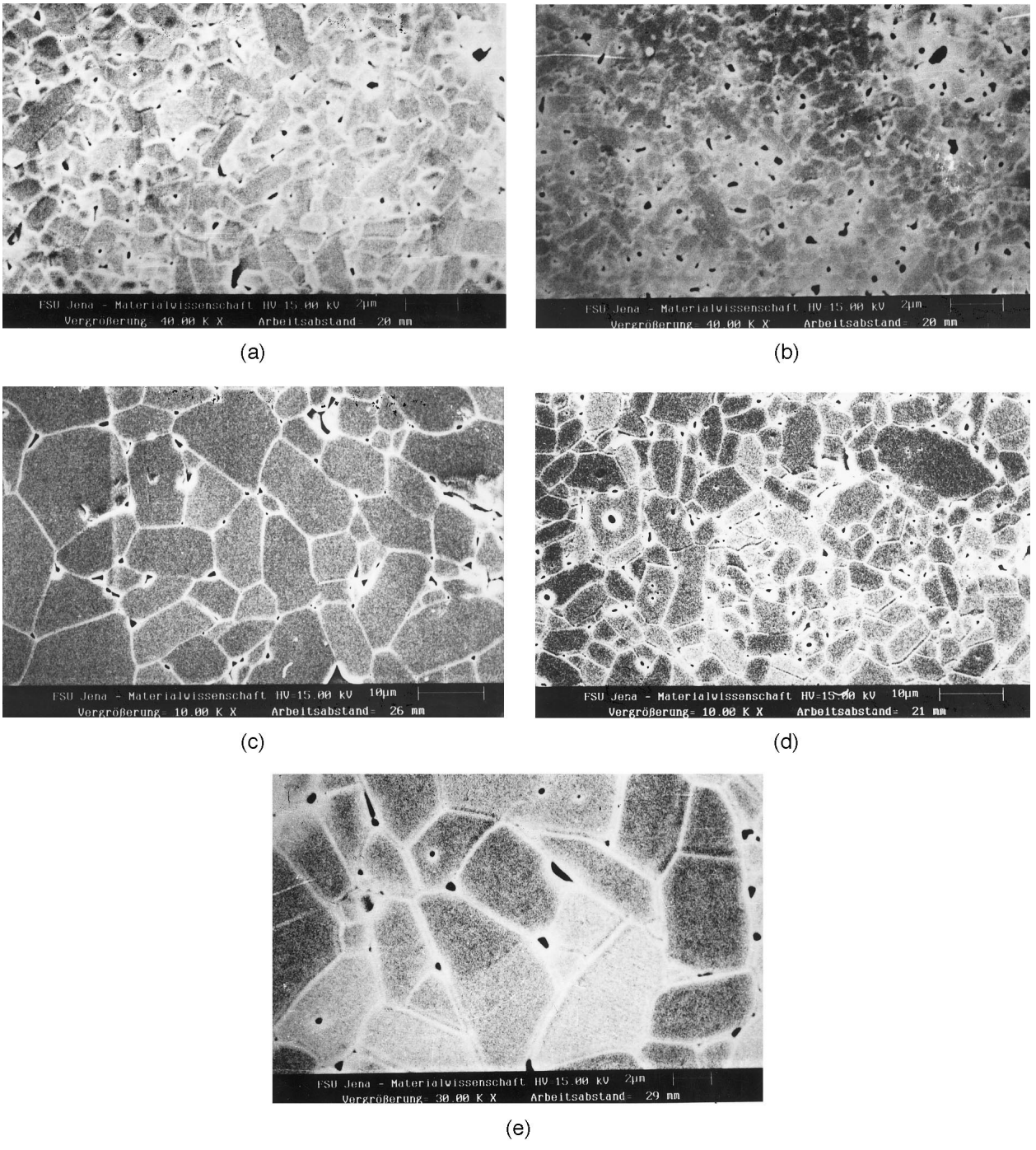

Fig. 9. SEM of alumina bodies isostatically pressed under 600 MPa, fired at different temperatures: (a) A_3 bodies fired at 1600°C; (b) A_4 bodies fired at 1600°C; (c) A_3 bodies fired at 1650°C; (d) A_4 bodies fired at 1650°C; (e) A_3 bodies fired at 1700°C.

densified. The relative density varied between 69 to 89% of the TD when fired between 1450 to 1700°C, Table 1.

SEM of all processed bodies in Figs. 8 and 9 show a general feature indicating the very fine nature of oxide grains; less than 1 µm. Some of the grains are arranged preserving the ring and branch structure of the former resin. Therefore, there arises patches of these fired grains totally densified giving the appearance of one big grain. While the grains forming the branches are arranged in a more or less curvilinear form there around these patches leaving some pores. Pores are very fine within the patch indicating the center of the former rings and they are intragranular. Also pores, are formed between the patches and branches as a result of the adherence of some of the grains. No intergranular pores were identified. SEM of A_3 bodies processed under

300 MPa and fired at 1450 and 1550°C are shown in Fig. 8. Grains are about 0.5 μm in size with minute intragranular pores. Better densification was achieved in specimens isostatically processed under 600 MPa from A_3 fired at 1600°C, Fig. 9. Grains are uniform in shape, prismatic with a size less than 2 μm. Grain growth took place in specimens fired at 1650°C and was exaggerated in specimens fired at 1700°C. Microstructure of bodies from A_4 processed under 300 MPa and fired at 1450°C show interconnection between the massive patches. Branches in some points of adherence leave pores, penny shaped or crescent like Fig. 8. The number of pores is greater than in A_3 specimens processed and fired under the same conditions. Also, specimens of A_4 processed under 600 MPa and fired at 1650°C showed porous nature compared with A_3 ones.

Aluminium hosted in the resin coordinated in both tetrahedral and octahedral sites is evident from IR spectrum [15]. Therefore, on calcination the octahedrally coordinated aluminium form the nuclei for α-alumina formation. So, actually the powder calcined at 700°C contain both phases γ and θ. On further heat treatment the γ phase transforms to θ then to α.

According to Bowen et al. [16] the initial α content is the predominant factor in lowering the transformation and sintering temperature of γ-alumina. This is in agreement with the seeding of alumina precursors with α-particles [17] whereas α-particles act as low energy sites for nucleation and growth of the α-phase by solid state phase epitaxy.

Bodies processed from alumina prepared by the present method did not reach complete densification. A maximum of 93% of TD was reached for bodies processed from powders calcined at 700°C and processed either under 300 MPa and fired at 1550°C or processed under 600 MPa and fired at 1650°C. Meanwhile firing at 1700°C showed growth of the grains and the density decreased to 90.93 and 88.45% for A_3 and A_4, for powders processed under 600 MPa, respectively. Coble [18] proposed four stages for the sintering process. In the first stage, the loosely packed particles are characterized by low initial relative density of 0.6. Pores are interconnected in a network and the grain size does not change. In the second stage, sintering and grain growth manifest themselves with pore structure essentially the same. In the third stage pores start to coalesce leading to 95% TD. The final stage is manifested in migration of grain boundaries causing pores to be isolated in the grains. Meanwhile grain growth continues.

Accordingly, in the present study, it is clear that proper sintering taking place finished the first and the second stages of sintering and is towards the end of the third stage, whereas, the relative density achieved did not exceed 93% TD.

Usually densification of alumina is better achieved either through additives as MgO that inhibits grain growth or by firing in an atmosphere of oxygen or hydrogen as recommended by Coble [18]. This will be considered in future work.

4. Conclusion

Nano-meter size, uniform spherical, α-alumina particles can be prepared via the present method. Bodies processed from the powders reached 93 to 94% TD when processed by cold isostatic press under 300 and 600 MPa, and fired at 1550°C. Firing at 1770°C caused grain growth and density was lowered to 90% TD.

Acknowledgements

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