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Effect of the starting Al_2O_3 and of the method of preparation on the characteristics of Li-stabilized β''-Al_2O_3 ceramics

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The influence of the morphology and the size of the particles of various types of starting Al_2O_3 material on the synthesis and characteristics of Li-stabilized β''-Al_2O_3 ceramics have been investigated. The use of highly dispersed oxides makes it possible to attain higher densities in the fired ceramic bodies due to their higher reactivity. In the case of oxides obtained from ammonium alum, the degree of dispersion and the reactivity may be increased by raising the amount of γ-Al_2O_3 up to a certain limit. Alumina prepared from $Al_2(OH)_5NO_3$ by slurry solution spray-drying also gives satisfactory results despite its lower degree of dispersion. This is connected with the morphology of the particles. In the case of synthesized materials containing an insufficient amount of β-Al_2O_3–$NaAlO_2$ eutectic, high densities may also be achieved by applying a two-step firing schedule at temperatures above the melting point of the eutectic.

1. Introduction

The practical application of polycrystalline β-alumina membranes as solid electrolyte in the sodium–sulphur battery requires optimization and control of their electrochemical and physical properties, such as density, ionic conductivity, mechanical characteristics, corrosion resistance, etc. These properties depend on the crystal structure (at the unit cell level) of the constituting β-alumina phases and on the microstructure of the membranes (i.e. on the grain size and morphology of the crystallites, on the presence of pores, on the bulk porosity, etc.). In turn these characteristics depend on factors such as the nature and state of the starting Al_2O_3 material used in the synthesis process, the phase composition, the degree of dispersion of the synthesized product and on the firing schedule. It is therefore clear that the optimization of the practically important properties of the β-alumina membranes must be based on a careful analysis of the correlations existing between the experimentally selected conditions and the observed characteristics.

Since it has been recognized that the properties of the membranes depend both on their intra- and intergranular structure, recent research work has been concentrated in two fields: (i) investigation of the "local" structure of β-alumina single crystals by modern physical methods (X-ray diffuse scattering and laser Raman scattering, resonance methods, etc.), a trend which has been well summarized by Colomban [1]; (ii) study of the effect of the microstructure of the membranes on their physical and electrochemical properties. The resistivity/microstructure relations in lithia-stabilized β''-Al_2O_3 have been thoroughly studied by Virkar *et al.* [2], who proposed a model which attempts to explain the dependence of resistivity on grain size. Youngblood *et al.* [3] studied the effect of phase composition and grain size on conduction. Whalen *et al.* [4] also examined the properties/microstructure relations in β''-Al_2O_3 ceramics. These problems were also discussed by Kinsman and Tennenhouse [5], De Jonghe [6] and Bugden and Duncan [7].

The present paper deals with the influence of

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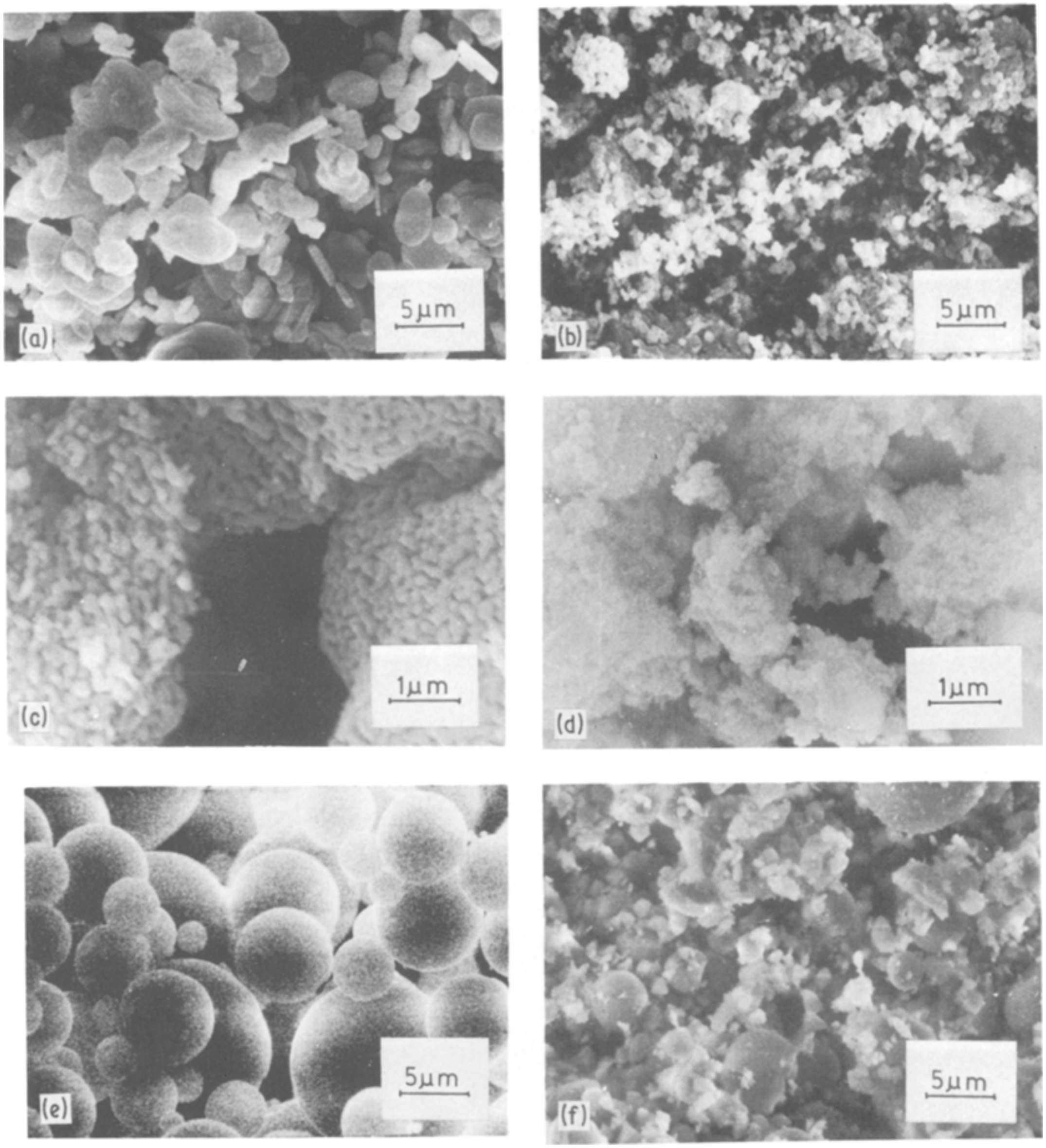

Figure 1 Scanning electron micrographs of the starting Al_2O_3 used as: (a) α-Al_2O_3 (Material A) after milling (× 1740); (b) α-Al_2O_3 (Material M) after milling (× 1740); (c) α-Al_2O_3 (Material C) (× 8700); (d) $\alpha + \gamma$-Al_2O_3 (Material C) (× 8700); (e) α-Al_2O_3 (Material H) (× 1740); (f) α-Al_2O_3 (Material H), after milling (× 1740).

the nature and state of the starting alumina used in β-alumina synthesis on the morphology of β-alumina prepared from them and on the properties of fired membranes.

2. Experimental procedure

The following aluminas were used in order to elucidate the effect of the nature of the starting Al_2O_3 material on the behaviour during sintering of the corresponding compositions of β''-Al_2O_3 and on the properties of the membranes:

(1) α-Al_2O_3, (99.95%) commercial Alcoa International Co., USA (Material A);

(2) α-Al_2O_3, (99.95%), prepared from commercial γ-Al_2O_3 Merck, FRG (Material M);

(3) α-Al_2O_3 and $\alpha + \gamma$-Al_2O_3 (99.98%) prepared from ammonium alum (Material C);

(4) α-Al_2O_3 (99.97%) prepared from $Al_2(OH)_5NO_3$, according to Yanakiev [8] (Material H).

Material A (Fig. 1a) was used after 48 h of dry vibration milling followed by 5 h of friction milling in acetone.

TABLE I

Number	Characteristics	Method of preparation					
		Zeta-process				SSSD	
		Al_2O_3 (C)		Al_2O_3 (M)	Al_2O_3 (A)	Al_2O_3 (C)	Al_2O_3 (H)
	Starting Al_2O_3						
1	Polymorph	$\alpha + \gamma$	α	α	α	α	α
2	Average grain size (μm)	< 0.1; 0.3	0.3	1.0	3.5	0.3	2.5
3	BET specific surface area ($m^2 g^{-1}$)	25.9	5.6	2.8	1.0	5.6	3.8
	Synthesized powders						
4	BET specific surface area ($m^2 g^{-1}$)	6.4	2.9	1.0	1.0	3.5	2.5
5	Approximate β''-Al_2O_3 content (wt %)	90	90	70	40	50	40
	Pressed unfired samples						
6	Green density ($g\,cm^{-3}$)	1.82	1.92	1.95	1.99	1.89	2.13
7	Maximum pore radius (μm)	0.13	0.18	0.25	0.25	0.15	0.30
8	Pore radius distribution (%)						
	0–0.1 μm	0	0	0	0	0	0
	0.01–0.05 μm	18	5	10	0	7	8
	0.05–0.10 μm	72	35	10	3	31	22
	0.10–max. radius, μm	10	60	80	97	62	70
	Fired samples						
9	Approximate β''-Al_2O_3 content (wt %)	100	100	80	50	80	60
10	Fired density ($g\,cm^{-3}$)	3.17	3.14	3.03	2.96	3.20	3.20

Material M (Fig. 1b) was prepared by transforming γ-Al_2O_3 to α-Al_2O_3 by heating at 1280° C for 5 h with subsequent milling as in the previous case.

Materials of the Type C were prepared by melting ammonium alum at 300° C with subsequent thermal decomposition up to 1050° C for 15 h. This procedure leads to the formation of γ-Al_2O_3. The α-polymorph was obtained by heating γ-Al_2O_3 at 1280° C for 5 h (Fig. 1c). The α- + γ-Al_2O_3 material was prepared by mixing and homogenizing the pure α- and γ-polymorphs in appropriate proportions (Fig. 1d).

Material H was obtained by spray-drying an aqueous solution of $Al_2(OH)_5NO_3$ (aluminium hydroxynitrate) with subsequent thermal decomposition. The Al_2O_3 content of the solutions ranged from 8 to 12 wt % and the pH was maintained at 4 ± 0.2. Spray drying was performed with a Niro Atomizer Mobile Spray Drying Minor Unit at a pressure of 5 atm (35 000 rpm). The temperature at the inlet was 300 to 320° C and at the outlet 110 to 120° C.

Thermal decomposition of the nitrates in the dried material was effected at 800° C. The transformation of the amorphous product thus obtained into α-Al_2O_3 was carried out at 1280° C for a few hours. In order to destroy the globular structure of the particles (Fig. 1e) α-Al_2O_3 was subjected to the same milling procedures as Material A (Fig. 1f).

The characteristics of the above oxides, as well as those of the corresponding synthesized materials and β-alumina ceramic bodies, are summarized in Table I.

Batches with nominal composition 9.0 wt % Na_2O, 0.75 wt % Li_2O and 90.25 wt % Al_2O_3 were prepared from these oxides. Two methods of preparation were used:

(1) "Zeta process" [9, 10] in which sodium and lithium containing components are separately obtained by grinding and homogenization of $Na_2CO_3 + Al_2O_3$ and $Li_2CO_3 + Al_2O_3$ mixtures taken in the appropriate proportions:

$$Na_2O(Li_2O) : Al_2O_3 = 1 : 5.$$

Synthesis at 1260° C leads to the formation of $Na_2O{\cdot}5Al_2O_3$ and $Li_2O{\cdot}5Al_2O_3$ (zeta-lithium aluminate). After mixing in appropriate proportions, deagglomeration and homogenization, a mechanical mixture of the two components is formed which is used for the fabrication of membranes. Starting Materials A, M and C were used for this process.

(2) Slurry solution spray-drying process (SSSD process). α-Al_2O_3 (Materials C and H) suspensions in Na_2CO_3 and $LiNO_3$ solutions, taken in proportion corresponding to the nominal composition, were spray dried and subjected to subsequent synthesis at 1250° C [9, 10]. Prior to the preparation of the suspension and after synthesis the solid compounds were subjected to de-agglomeration and homogenization. Starting Materials C (pure α-Al_2O_3) and H were used for this process. Such experiments were also performed with Materials A and M but are not included in Table I.

These materials yielded lithia-stabilized β''-Al_2O_3 and were used for the fabrication of membranes of two types in the shape of closed-end tubes with the following dimensions: (i) length 100 mm, outer diameter 11 mm, wall thickness 1.5 mm, and (ii) 200 mm × 38 mm × 2 mm, respectively. Forming was carried out by isostatic pressing at $4000\,kg\,cm^{-2}$. Green density and bulk porosity were determined by mercury penetration porosimetry.

The formed tubes were encapsulated in cylindrical containers made of β''-Al_2O_3 [11] or platinum and were thermally treated at 950° C for 3 h prior to firing. The firings were performed in air in a tubular furnace by a pass-through technique at a given velocity with concomitant rotation of the containers with the samples [11]. The temperature and the sintering times were varied between 1580 and 1630° C and 30 and 4 min, respectively. Two firings were performed according to a two-step firing schedule. The first, shorter step was at a higher temperature and the second one, for a longer time, at a lower temperature. No differences in the chemical composition of the ceramics fired in β''-Al_2O_3 and platinum capsules were detected.

The fired samples were studied with respect to phase and chemical composition, density, resistivity and microstructure.

The phase composition was determined by X-ray diffraction. The approximate quantitative estimate of the relative amounts of β''- and β-Al_2O_3 was based on a comparison of the intensity ratio of the $2\,0\,\bar{2}.1\,0$ reflection of β''-Al_2O_3 and $2\,0\,\bar{2}\,6$ and $2\,0\,\bar{2}\,7$ reflections of β-Al_2O_3.

Chemical analysis was performed by atomic absorption spectrophotometry (soda and lithia contents were determined).

Sintered density was determined pycnometrically in xylene.

Resistivity was measured axially at 320° C at 50 Hz. The contacts consisted of an eutectic melt of $NaNO_3/NaNO_2$ between the sample and the measuring circuit.

The microstructure of the samples was examined in thin sections by means of optical polarization microscopy in transmitted light. The relative portion of the coarse-grained fraction (larger than 5 μm) was measured by image analysis electronic equipment.

3. Results and discussion

The results obtained from the study of the five materials are summarized in Table I.

The highly dispersed oxides of Type C (specific areas up to $25.9\,m^2\,g^{-1}$) when subjected to synthesis according to the "zeta-process" yield β''-Al_2O_3 which is also highly dispersed (specific surface area $6.45\,m^2\,g^{-1}$). This makes it possible to achieve higher fired densities ($3.17\,g\,cm^{-3}$ compared to about $3\,g\,cm^{-3}$ obtained from the less dispersed Materials M and A). Obviously these oxides are more reactive. This is also indicated by the increased rate of synthesis affecting the phase formation process. Indeed in this case only β''-Al_2O_3 is identified, whereas in Materials M and A commensurate amounts of β-Al_2O_3 (about 60%) are formed.

The degree of dispersion and the reactivity of the oxides of Type C may be increased at the expense of the increase of the γ-polymorph content but this is possible only to a certain extent because planar defects are inherited by the structure of the synthesized β-alumina phases from the initial γ-Al_2O_3 [12].

The compositions prepared by the SSSD process from oxides C and H generally bring about a higher density of the fired ceramic samples than those obtained by the "zeta-process". This is due to the fact that the materials synthesized according to the first process have a higher β-Al_2O_3 content (up to 50 to 60%). With a composition containing a higher amount of Na_2O corresponding to a β''-Al_2O_3 final product, an appreciable amount of β-Al_2O_3 in the synthesized material requires the

TABLE II

Synthesized material number	Starting material and method of preparation	≈ β''-Al_2O_3 after synthesis (%)	Firing schedule		Approximate β''-Al_2O_3 content after firing (%)	Fired density ($g\,cm^{-3}$)	Resistivity at 320° C (ohm cm)	Microstructure	
			T (° C)	Time (min)				Average size of large crystals (μm)	Amount of large crystals (%)
1.1		90	1630	20	100	3.12	6.2	180	49
1.2	$\alpha + \gamma$-Al_2O_3		1620	30	100	3.14	5.5	150	32
1.3	"C"		1620	20	100	3.15	6.1	80	31
1.4	Zeta		1620	10	100	3.17	9.9	100	45
1.5			1620 1600	3 9	100	3.18	11.8	5	0
2.1	α-Al_2O_3	90	1620	30	100	3.15	10.3	100	27
2.2	"C"		1620	25	100	3.13	10.5	70	17
2.3	Zeta		1620	10	100	3.14	33.7	5	0
2.4			1600	13	100	3.10	31.4	5	0
3.1		50	1630	20	100	3.06	7.4	100	–
3.2			1620	4	60	3.18	37.9	5	0
3.3	α-Al_2O_3		1620	7	80	3.20	27.7	5	0
3.4	"C"		1620	10	80	3.19	21.7	150	5
3.5	SSSD		1600	10	80	3.17	27.3	30	4
3.6			1590	17	80	3.17	25.8	130	17
3.7			1580	30	100	3.12	6.6	200	29
4.1		40	1620	4	40	3.16	35.0	5	0
4.2			1620	7	60	3.20	29.5	5	0
4.3	α-Al_2O_3		1620	10	70	3.20	24.9	5	0
4.4	"H"		1600	10	60	3.18	26.7	15	4
4.5	SSSD		1590	17	70	3.20	19.8	25	11
4.6			1580	30	80	3.21	6.6	15	14
4.7			1620 1600	3 9	80	3.205	11.4	50	–

presence of $NaAlO_2$. It is well known that densification may be achieved at relatively low firing temperatures thanks to the transient formation of the β-Al_2O_3 + $NaAlO_2$ eutectic liquid [9]. This eutectic is visible on the phase diagram for the binary system Na_2O–Al_2O_3 by Weber and Venero quoted by Kummer [13].

It should be noted that in the case of oxides C when the synthesis is performed in the presence of lithia the amount of β-Al_2O_3 increases considerably (see Table I, Line 5). Apparently, at these temperatures, lithia exerts a stabilizing effect on β-Al_2O_3, whereas at higher temperatures (1400 to 1650° C) it stabilizes β''-Al_2O_3, making the phase conversion $\beta \rightarrow \beta''$-$Al_2O_3$ possible [14]. The mechanism of these two effects and the connection between them are still unclear and require additional study.

As expected, the pore-size distribution (Table 1, Item 8) of the green body has an appreciable influence on the density of the final product (Item 10). The SSSD process seems to be less sensitive to this influence because of the transient liquid formation.

The results given in Table I for the fired density of β''-Al_2O_3 samples prepared from the various starting aluminas show that sufficiently high values are reached in the case of oxide C (pure α- and mixed α- + γ-polymorphs) and Type H. In contrast, low fired densities are observed when aluminas M and A are used, prepared by the "zeta-process" and SSSD (the data referring to the latter are not included in the table).

This is why only Materials C and H were used in the subsequent investigations.

Comparison of the data in Table II referring to Materials 1, 2 and 3 obtained from oxide C by the SSSD and zeta processes as indicated confirms in general that the increase in firing time or in firing temperature leads to the formation of larger crystals and to an increase of their relative amounts, as described elsewhere [9, 10]. Typical microstructures of fired ceramic samples are shown

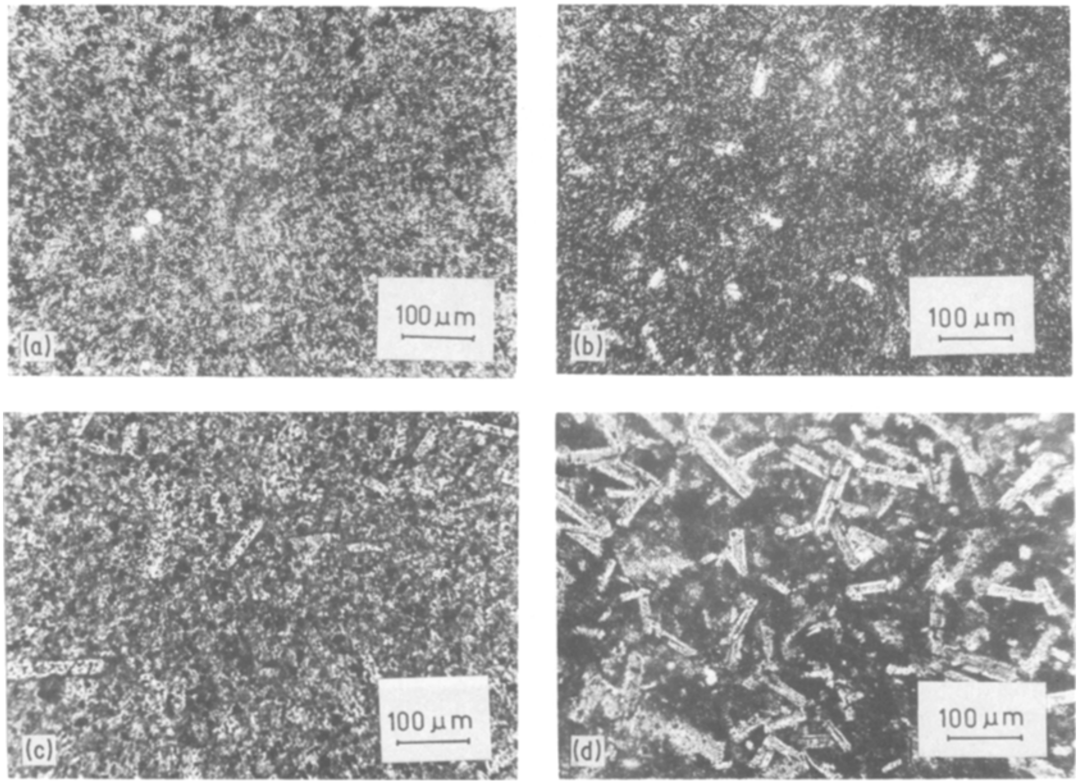

Figure 2 Typical microstructures of fired Li-stabilized β''-Al_2O_3 membranes. Micrographs taken in transmitted polarized light. (a) Microlitic (cf. items 1.5 in Table II); (b) microlitic with porphyritic individuals with irregular outlines (cf. item 4.6 in Table II); (c) microlitic with porphyritic individuals with well-formed shapes (cf. item 2.1 in Table II); (d) porphyritic, with large individuals embedded in a microlitic matrix (cf. item 1.4 in Table II).

in Fig. 2a to d. Using the transient effect firing times can be shortened. In this case the densification rate is considerably higher than the rate of phase conversion:

$$\beta\text{-}Al_2O_3 + NaAlO_2 \rightarrow \beta''\text{-}Al_2O_3.$$

This is seen for Material 3 fired for 4 to 10 min at 1620° C. Maximum density is achieved at a firing time of 7 min. This indicates that for a firing time of 10 min the liquid formation mechanism of densification ceases to exert a noticeable influence and at firing times of less than 4 to 5 min the process is prematurely interrupted. Upon transient liquid sintering, fine-grained structures and high densities are accompanied by an increased resistivity. An additional thermal treatment is usually required for the completion of the phase conversion and the improvement of the intergrain contacts resulting in a decrease of resistivity.

This effect is considerably weaker in the case of Materials 1 and 2, which contain insufficient amounts of eutectic mixture (i.e. low β-Al_2O_3 content, see Table I). However, the combination of firing with a subsequent thermal treatment at temperatures higher than the eutectic point in a single two-step process (1620° C for 3 min and 1600° C for 9 min) also gives good results in the case of Material 1. (Note also the decisive improvement of the microlitic structure, Table II, Items 1 and 5 compared with Items 1 and 4).

Material 4, obtained from alumina Type H, shows a different behaviour. From Table II it is seen that satisfactory characteristics are obtained within a wide range of conditions (temperature 1580 to 1620° C and firing times from 4 to 30 min). When the conditions are varied within these limits the microstructure does not change drastically whereas resistivity decreases with the increase of the firing time which plays a dominant role, irrespective of the temperature. These particular features of the material are determined by the lower degree of dispersion and the morphology of the particles of oxide Type H which are initially hollow globules with a diameter of 5 to

10 μm. After de-agglomeration the destructed globules have a size of 2 to 3 μm. The lower degree of dispersion decreases the rates of densification, phase conversion and crystallization during firing.

4. Conclusions

(1) The influence of the morphology and the particle size of the starting aluminas on the synthesis and firing processes of Li-stabilized β''-Al_2O_3 ceramic bodies was investigated.

(2) The relationship between the degree of dispersion of the starting aluminas and the density of fired β''-Al_2O_3 membranes was confirmed. This is connected with the reactivity of the starting materials.

(3) It was shown that the reactivity of alumina prepared from ammonium alum as well as the density of the ceramics increases when a certain amount of γ-Al_2O_3 is added to α-Al_2O_3.

(4) It was found that Li_2O stabilizes β-Al_2O_3 at synthesis temperatures (about 1260° C) whereas at firing temperatures (1400 to 1650° C) it stabilizes the β''-phase.

(5) The use of starting α-Al_2O_3 prepared by spray-drying of an aqueous solution of $Al_2(OH)_5NO_3$ leads to satisfactory characteristics of the fired bodies.

(6) When the synthesized compositions do not contain a sufficient amount of eutectic mixture, higher densities may be achieved via a single two-step firing schedule at temperatures above the eutectic point.

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