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Andrzej SZYMAŃSKI*, Władysław WŁOSIŃSKI*

THE TRANSFORMATION OF THE PHASE COMPOSITION OF POLYCRYSTALLINE CERAMIC MATERIALS DURING METASOMATIC RE-SINTERING

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Abstract. Taking as an illustrative case a ceramic material made up of polycrystalline $\alpha\text{-}Al_2O_3$ which was subjected to $metasomatic\ sintering\ at\ 2000\ K$ in the presence of sodium aluminate NaAlO2, the authors demonstrate the possibility of complete transformation by diffusion of compact polycrystalline ceramic $\alpha\text{-}Al_2O_3$ into $\beta\text{-}Al_2O_3$ (Na2O·11Al2O3). The resultant material has an ionic conductivity of $2.7\cdot10^{-1}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ at 570 K. The preservation of compact, non-porous structure of the material despite a 20% increase in volume was possible due to the fact that $\beta\text{-}Al_2O_3$ retains the tabular habit of corundum crystals. Sodium aluminate (Na2O·11Al2O3) is pseudomorphous after corundum. The material obtained meets all the requirements as a solid electrolyte used in Na-S cells.

INTRODUCTION

Ceramic materials are obtained by partial or complete vitrification of a set of mineral components, or by inhibiting of the sintering process at a specified moment. It follows, therefore, that the whole process rests on a series of solid-state reactions and, if appropriately programmed, yields a ceramic material of the desired phase composition and structure. It is also interesting to note that a large number of microstructures with different properties may be obtained from batches of similar composition. Due to this, it is generally held that ceramics is the chemistry of inhibited processes.

Due to considerable divergence in opinions concerning the nomenclature of ceramic materials (Szymański 1976), certain option is allowed in this respect. Assuming that the name of a material is to define briefly its kind and composition, the present authors will use furtheron the name ceram suggested by E. Görlich, which has the same connotation in ceramography as rock in petrography or metal in metallography. The word ceram denotes that the inorganic non-metallic material is obtained by synthesis, whereas

^{*} Research and Production Centre of Semiconductor Materials, 02-637 Warszawa, ul. Konstruktorska 6, Poland.

the preceding word or words define its composition and approximate structure, e.g. corundum ceram. The terms alundum ceramic material or alundum ceramic, which are generally used, afford no information on the material.

If ceramics is defined as the chemistry of inhibited processes, it is obvious that a process may be prolonged and, consequently, the properties of the resultant ceram changes as desired. The first materials subjected to secondary heat or photochemical treatment were glass cerams (Stooky 1959, McMillan 1964). Depending on the intensity of the process, re-heating or irradiation of glass cerams containing the nuclei of crystals results in controlled devitrification, yielding ultimately a wide spectrum of new glass-ceramic cerams with a cryptocrystalline structure and properties modified by the amount and kind of mineral components, such as cristobalite, pyroxenes, and others, crystallizing in the ceram. These materials have been given different names (devitrificates, sittals, glass-ceramic materials) which are to render their intermediate position between glass cerams and the porcelain-type polycrystalline cerams. The cryptocrystalline structure of devitrified glass cerams increases their hardness by two Mohs degrees relative to the initial glass ceram (Szymański 1973). This widens considerably the range of application of these materials (Mc Millan 1964; Szymański. Włosiński 1976).

As demonstrated hereafter, polycrystalline cerams can be heat-treated again with simultaneous introduction by diffusion of specific cations into the structure of minerals making up the initial ceram. In the process of metasomatic re-sintering the phase composition and the structure of the ceram can be changed in such a way that the product would possess the desired functional properties. A monophase corundum ceram made up of polycrystalline α -Al₂O₃ with a small amount of intercrystalline aluminium—high glassy phase was selected for the present investigations. The material in question is formed from aluminium oxide obtained in Bayer process as aluminium hydroxide which is transformed by calcination into α -Al₂O₃. After grinding to a grain-size $< 3 \, \mu m$ and compressing at a pressure of about 3000 kG/cm², the material is heated in a gas furnace at 2070 K, yielding a typical corundum ceram of a hardness between 9.1—9.2 in Mohs scale and a porosity < 0.01. It is used as dielectric in electronic industry or as a construction and tool material in machine building industry.

The purpose of this paper was to investigate the possibility of transformation of α -Al₂O₃ into β -Al₂O₃, being actually sodium aluminate Na₂O·11Al₂O₃, in the process of re-sintering. β -Al₂O₃ is a prospective material which can find application in one-fluid sodium-sulphur cells (Miles, Wynn-Jons 1971; Kawalcami *et al.* 1975; Demot 1971; Seltzer, Jaffee 1974) as a solid electrolyte of high unipolar ionic conductivity induced by migration of Na⁺ ion. The cell consists of liquid sodium as the cathode, the solid electrolyte β -Al₂O₃ as interlayer and sulphur-saturated graphite adhering to aluminium or steel which acts as the anode carrying away the current. At about 570 K, when a complete circuit is made, liquid sodium migrates through the electrolyte to sulphur according to the reaction:

$$Na \rightarrow Na^+ + e (Na^+ diffuses through \beta-Al_2O_3)$$

$$2Na^+ + S + 2e \rightarrow Na_2S$$

and then

$$Na_2S + 3S \rightarrow Na_2S_4$$
,
or $Na_2S + 4S \rightarrow Na_2S_5$.

After the electromotive force of the cell drops down to ≤ 1.8 , the cell is recharged (sodium returns). It is claimed that up to 600 cycles the structure of the solid electrolyte β-Al₂O₃ is not subject to changes (this is true of a monocrystalline material). Being impermeable to liquids and gases and heat-resistant up to high temperatures, β-Al₂O₃ is a material specifically useful for cells operating at elevated temperatures. The conductivity of \(\beta - Al_2O_2 \) increases with a rise in temperature and, according to the data published by other authors, at 570 K it attains a value of $3 \cdot 10^{-1} \Omega^{-1} \text{cm}^{-1}$ for a monocrystal (Miles, Wynn-Jons 1971), $0.35 \cdot 10^{-1} \Omega^{-1} \text{cm}^{-1}$ for pure polycrystalline cerams (Demot 1971), or 1.88 and $2.61 \cdot 10^{-1} \Omega^{-1} cm^{-1}$, respectively, for polycrystalline cerams with admixtures of MgO and Y₂O₃ (0.3—3.0%) (Kawalcami et al. 1975). It is interesting to note that, in contrast to monocrystals, the cerams show substantial variations in conductivity in the temperature range of 570—670 K. This is due to unequal internal porosity of cerams which were formed from aluminium oxide transformed into β -Al₂O₃ prior to formation, or from a mixture of α -Al₂O₃ with sodium aluminate NaAlO2. The transformation by diffusion of the compact corundum ceram obtained by firing at 2070 K into β-Al₂O₃ should guarantee the preservation of the compact structure, whereby the conductivity of a polycrystalline ceram will be close to that of a monocrystal.

EXPERIMENTAL

Two batches of ceramic materials were prepared: pure aluminium oxide α -Al₂O₃ (99.5 Al₂O₃) of grain size $< 3\,\mu m$ and the specific surface area 5080 cm²/g (A), and the same oxide with a 2 mole % addition of CaO to facilitate sintering (B). The batches disks of a size ϕ 30 \times 4 mm were for-

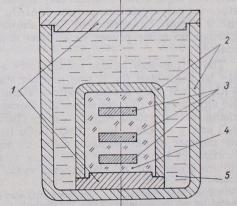


Fig. 1. The position of plates of α -Al₂O₃ ceram subjected to metasomatic re-sintering in the furnace $1-\alpha$ -Al₂O₃ ceram lids, $2-\alpha$ -Al₂O₃ ceram crucibles, $3-\alpha$ -Al₂O₃ ceram plates, $4-\alpha$ -Al₂O₃ + NaAl₂O₃ powder, $5-\alpha$ -Al₂O₃ powder

X-ray diffraction data for β-Al₂O₃

med at a pressure of 3000 kG/cm² and fired at 2070 K to give corundum ceram. The fired disks were placed in a corundum ceram crucible together with $\alpha\text{-}Al_2O_3$ powder mixed with NaAlO₂ powder in the ratio of 1:2 (Fig. 1). The sealed crucible was put into another crucible and the interspace filled with pure $\alpha\text{-}Al_2O_3$ powder. The batch thus prepared was resintered in a gas furnace in an atmosphere of air at 1900—2000 K for 24 h and held for 1 h at maximum temperature. Sodium from NaAlO₂ diffused into $\alpha\text{-}Al_2O_3$, transforming it into sodium aluminate Na₂O·11Al₂O₃.

RESULTS

The cerams obtained upon metasomatic re-sintering were subjected to X-ray examinations in a Rigaku-Denki apparatus and ceramographic analyses in a scanning microscope (Jeol 4A). Moreover, their ionic conductivity was investigated *. After re-sintering the samples showed an increase in diameter of 20%, corresponding approximately to the difference in the crystal structure density between α and β -Al₂O₃.

Table 1 presents the results of X-ray examinations of sample A, along with the ASTM data and those reported by some other authors (Dyson, Johnson 1973). The above results substantiate the inferences emerging from the increase in volume, viz. that the corundum ceram underwent complete structural transformation into sodium aluminate β -Al₂O₃. The latter ceram has been found to contain no α -Al₂O₃ which made up the initial material.

Ceramographic investigations have revealed that samples A and B have a compact but different structure (Phot. 1a-d). The photographs show the samples at magnifications of 1000 and $3000\times$.

Conductivity measurements were performed on 3 mm thick plates placed in a specially designed measuring device made of brass. A plate was sealed between two flanged tubes containing liquid sodium. Direct current was passed through the plate and sodium, and the current intensity and voltage were measured. Knowing the dimensions of the working part of the plate, the conductivity of the material was calculated, neglecting the resistance of sodium and wires (Table 2). The obtained values for conductivity are high, being considerably higher than those reported in the literature for polycrystalline cerams $\beta\text{-Al}_2\text{O}_3$. It is worth noting that the ceram with a 2 mole % addition of CaO shows a markedly lower conductivity although no other phases have been detected in either of the materials studied.

The differences in the conductivity and structure of the two cerams may be accounted for if one realizes that the name β -aluminium oxide $(\beta-Al_2O_3)$ not only denotes sodium aluminate $Na_2O\cdot 11Al_2O_3$ but actually also embraces within its scope the isomorphic series of alkali aluminates arising in the system Al_2O_3-x-y (Table 3), in which $x-Na_2O$; K_2O ; Li_2O and y-CaO; MgO; SrO; BaO. In view of the similar ionic radii, any number of intermediate members showing a various degree of substitution in the structure may arise in this system because, except for lithium aluminate, all the others crystallize in the same class C6/mmc.

Sample A		After ASTM		After Dyson and Johnson (1973)	
d (Å)	I	d (Å)	I	d (Å)	I
5.63	9.1	5.7	30	0 0-0	_
4.83	1390191		_	4.732	2
4.46	aguate to	4.45	10	_	_
4.36	Best alternation	Antible - Lander	Se -tail		_
4.07	6.2	4.07	10		_
2.768	Description of the last	Mining — Indian	_	2.797	46
2.676	28.3	2.68	70	-	_
2.501		2.501	30	-	W 100 TO
2.41		2.41	30	_	-0
2.373			_	2.368	18
2.245		2.24	30		-
2.135		2.14	30	- 4 -	-
2.037	- 15.6	2.03	30	_	_
2.006		_		_	-
1.936		1.936	30	_	Page -
1.837		1.848	30	_	_
_	4 10 10 10 10	1.743	30	_	_
1.649		1.651	10	_	-
1.615			4	1.615	10
1.594	Colonia Colonia	1.591	70	_	-
1.564	8.0	1.563	30	_	
		1.483	30	-	-
1.409	500	Inus _ 25	_	1.412	24
1.402	30.5	1.402	100	-100	
1.392	2000000	saot wed		1	-
1.360	ones \$10	1.369	50		0.00 - 9
1.340	OB = (80	(2002) <u>—</u> 03	- *	-	-

When pure α -Al₂O₃ was used as the initial material (ceram A) unoriented Na₂O·11Al₂O₃ crystals with a platy habit were obtained, forming a subtle network of auto- and hipautomorphic needles. A completely different structure resulted from re-sintering of α -Al₂O₃ with an addition of CaO. The resultant β -aluminium oxide has a tabular habit and shows a xeno- and hipautomorphic form. Both habits are typical of aluminium oxide, the platy habit being characteristic of 3CaO·16Al₂O₃ or CaO·6Al₂O₃ and the tabular habit of corundum. β -Al₂O₃ is presumably pseudomorphous after corundum α -Al₂O₃.

The results for ionic conduction are much better in the case of pure sodium aluminate, the values obtained being much higher than those reported for polycrystalline cerams. This fact indicates that the batch with CaO yielding $\beta\text{-Al}_2\text{O}_3$ with a tabular habit and greater molecular density (cf. Table 3, items 2 and 5) in the unit cell has a markedly lower conductivity. It seems, therefore, that MgO or $K_2\text{O}$ have no negative effect on

Table 3

Ionic conductivity of β-Al₂O₃ cerams obtained by metasomatic re-sintering

dens.	Ionic conductivity (10 ⁻¹ Ω ⁻¹ cm ⁻¹)					
Tempera- ture	Ceram A	Ceram B	Pure ceram (after Miles, Wynn- -Jones 1971)	Ceram containing MgO (after Seltzer, Jaffee 1974)	Ceram containing Y_2O_3 (after Seltzer, Jaffee 1974)	β-Al ₂ O ₃ mono- crystal (after Demot 1971)
540	_	1.0			Light and the	
550		1.2				
560	2.7	1.7				
570	2.7	1.0	0.35	up to 1.88	up to 2.61	3.0

Structural data for α -Al₂O₃ and its alcaline variety β -Al₂O₃

No	Phase	Formula	Crystal system	Space	Molecules per unit cell (Z)
		2000			100
1	Alpha	Al ₂ O ₃	hexagonal	R3c	2
2	Sodium beta	Na ₂ O · 11Al ₂ O ₃	hexagonal	C6/mmc	1
3	Potassium beta	K ₂ O · 11Al ₂ O ₃	hexagonal	C6/mmc	1
4	Magnesium beta	MgO·11Al ₂ O ₃	hexagonal	C6/mmc	1
5	Calcium beta	CaO · 6Al ₂ O ₃	hexagonal	C6/mmc	2
6	Strontium beta	SrO · 6Al ₂ O ₃	hexagonal	C6/mmc	2
7	Barium beta	BaO · 6Al ₂ O ₃	hexagonal	C6/mmc	2
8	Lithium zeta	$\text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$	cubic	Fd3m	2

ionic conductivity (Table 3, items 3 and 4), whereas CaO, BaO, SrO and Li₂O admixtures are highly undesirable. A decrease in the density of the lattice by about 20%, resulting from incorporation of Na⁺ ions in the structure of corundum α -Al₂O₃, is limited by the amount of admixtures. This problem, however, requires thorough experimental studies combined with X-ray analysis (to determine the lattice parameters), as well as measurements of ionic conductivity of various modifications of the polymorphic β -Al₂O₃. Table 3 does not give the data for silver ceram β -Al₂O₃ discussed elsewhere (Seltzer, Jaffee 1974), the conductivity of which in similar to that of sodium ceram.

After measuring its ionic conductivity, ceram A was subjected to ceramographic analyses which failed to show any changes in its structure

CONCLUSIONS

- 1. It has been demonstrated that polycrystalline cerams can be transformed by metasomatic re-sintering in the presence of powdered material which is a carrier of the diffusing cation.
- 2. The resultant ceram retains high strength and the compact structure, due to which its ionic conduction $(2.7 \cdot 10^{-1} \Omega^{-1} \mathrm{cm}^{-1})$ at 570 K) is close to that of a β -Al₂O₃ monocrystal, exceeding the values reported by other authors. Not only the compact structure but also complete transformation of α -Al₂O₃ into β -Al₂O₃ is responsible for this high ionic conductivity. The materials discussed in other publications contained only 80—85% β -Al₂O₃ (Seltzer, Jaffee 1974).
- 3. It also seems possible to transform the polycrystalline corundum ceram α -Al₂O₃ by diffusion using other than aluminate sources of diffusion of sodium ions.
- 4. The above method of metasomatic re-sintering seems to be applicable to the transformation of other cerams of high ionic conductivity, such as ferrites of the magnetoplumbite type $(BaO\cdot 6Fe_2O_3)$ and hollandite $(Ba_2Mn_8O_{16})$, or to control the properties of cerams formed from garnet ferrites or cordierite.

REFERENCES

- COES L., 1971: Abrasives. Springer Verlag, Wien, 54.
- DEMOT D. S., HANCOCK P., 1971: Sodium ion transport in β-Al₂O₃. Proc. Brit. Ceram. Soc. 19, 193—205.
- DYSON S. J., JOHNSON W., 1973: Identification of β-alumina type phases. Trans. Brit. Cer. Soc. 72, 2, 49—55.
- KAWALCAMI T., INONE K., et al., 1975: Japan Kokei 75-88103.
- MILES L. J., WYNN-JONES J., 1971: Na transport trough β-Al₂O₃ membranes. Proc. Brit. Ceram. Soc. 19, 179—197.
- McMILLAN P. W., 1964: Glass—Ceramics. Acad. Press. London.
- SELTZER M. S., JAFFEE R. J., 1974: in: Defects and Transport in Oxides. Plenum Press. N.Y. 549.
- STOOKY K. S. D., 1959: Catalized crystalization of glass in theory and practice. Glasstech. Ber. 32 K, Heft 5.
- SZYMAŃSKI A., 1973: Określanie twardości minerałów i skał naturalnych i syntetycznych metodą ścieralności dynamicznej. Prace Inst. Chemii Nieorg. Polit. Wrocł., Studia i Materiały 3.
- SZYMAŃSKI A., 1976: Problem pojęcia struktury i tekstury w odniesieniu do tworzyw ceramicznych. Szkło i Ceramika, 6.
- SZYMAŃSKI A., WŁOSIŃSKI W., 1976: Ceramiczne narzędzia ścierne ze złączami termoelastycznymi. III Konf. Obróbka ścierna, Łódź, IX. 1976, 62—72.

O MOŻLIWOŚCI PRZETWARZANIA SKŁADU MINERALNEGO CERAMIKI POLIKRYSTALICZNEJ W PROCESIE WTÓRNEGO SPIEKANIA METASOMATYCZNEGO

Streszczenie

Na przykładzie spiekania metasomatycznego w 2000 K tworzywa ceramicznego zbudowanego z polikrystalicznego α -Al₂O₃ w obecności glinianu sodowego NaAlO₂ autorzy udowadniają możliwość pełnego dyfuzyjnego przetworzenia litej ceramiki polikrystalicznej α -Al₂O₃ w β -Al₂O₃ (Na₂O·11Al₂O₃). Pełna przebudowa struktury korundu w strukturę jedenastoglinianu sodu pozwoliła na otrzymanie tworzywa o przewodnictwie jonowym do 2,7·10⁻¹Q⁻¹cm⁻¹ w 570 K. Utrzymanie, mimo wzrostu objętości tworzywa o 20%, litej, nieporowatej struktury było możliwe dzięki zachowaniu przez β -Al₂O₃ tabliczkowatego pokroju kryształów α -Al₂O₃. Jedenastoglinian sodowy powstał tu jako pseudomorfoza po korundzie.

Otrzymane tworzywo spełnia wymagania stawiane stałym elektrolitom

stosowanym w ogniwach sodowo-siarkowych.

OBJAŚNIENIA FIGUR

Fig. 1. Sposób umieszczania płytek ceramu $\alpha\text{-Al}_2\mathrm{O}_3$ do wtórnego spiekania metasomatycznego

1 — przykrywki z ceramu α — Al₂O₃, 2 — tygle z ceramu α — Al₂O₃, 3 — płytki z ceramu α — Al₂O₃, 4 — zasypka α — Al₂O₃ + NaAlO₂, 5 — zasypka α — Al₂O₃

OBJAŚNIENIE FOTOGRAFII

Fot. 1. Struktury przełamów (SEM) ceramów β — Al_2O_3 otrzymanych w procesie wtórnego metasomatycznego spiekania α — Al_2O_3 α — próbka A, \times 1000, b — próbka B, \times 1000.

c — probka A, \times 1000, b — probka B, \times 1000 c — probka A, \times 3000, c — probka B, \times 3000

Fot. 2. Struktura przełamu (SEM) ceramu β — $\mathrm{Al_2O_3}$ po badaniu przewodnictwa jonowego

 $a - \times 600$, $b - \times 1800$

Анджей ШЫМАНЬСКИ, Владислав ВЛОСИНЬСКИ

О ВОЗМОЖНОСТИ ВИДОИЗМЕНЕНИЯ МИНЕРАЛЬНОГО СОСТАВА ПОЛИКРИСТАЛЛИЧЕСКОЙ КЕРАМИКИ ВО ВРЕМЯ ПРОЦЕССА ВТОРИЧНОГО МЕТАСОМАТИЧЕСКОГО СПЕКАНИЯ

Резюме

На примере метасоматического спекания при температуре $2000~{\rm K}$ керамического вещества построенного из поликристаллического $\alpha\text{-Al}_2{\rm O}_3$ в присутствии ${\rm NaAlO}_2$ авторы доказывают возможность полного диффиз-

ного преобразования компактной поликристаллической керамики α -Al₂O₃ в β -Al₂O₃ (Na₂O·11Al₂O₃). Полная перестройка структуры корунда в (Na₂O·11Al₂O₃) позволила получить вещество с ионной проводимостью до $2,7\cdot10^{-1}\Omega^{-1}$ см⁻¹ при температуре 570 К. Сохранение, помимо повышения объёма вещества на 20%, компактной, непористой структуры было созможно благодаря сохранению β -Al₂O₃ плиточной формы кристаллов α -Al₂O₃· (Na₂O·11Al₂O₃) образовался как псевдоморфоз после корунда. Полученное вещество отвечает всем требованиям, которые ставлятся постоянным электролитам в серно-натриеных батареях.

ОБЪЯСНЕНИЕ К ФИГУРЕ

Фиг. 1. Способ помещения плиток керама lpha-Al $_2$ O $_3$ при вторичном метасоматическом спекании

I — крышка из керама α -Al₂O₃, 2 — тигель из керама α -Al₂O₃, 3 — пластинки из керама α -Al₂O₃, 4 — присыпка α -Al₂O₃ + NaAlO₂, 5 — присыпка α -Al₂O₃

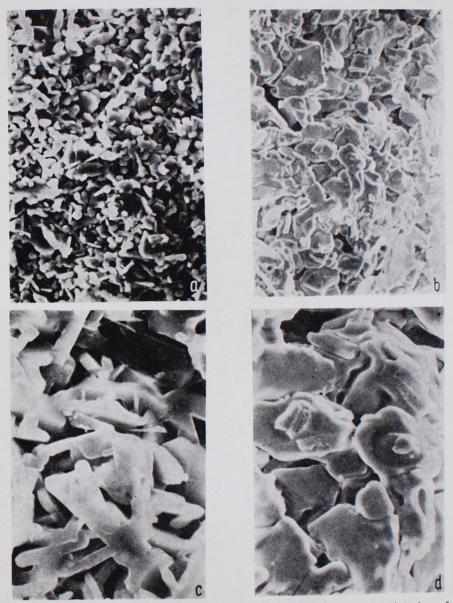
ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

Фот. 1. Структуры переломов (SEM) керамов β-Al₂O₃ полученных в процессе вторичного метасоматического спекания α-Al₂O₃

a — образец A, \times 1000, b — образец B, \times 1000, c — образец A, \times 3000, d — образец B, \times 3000

Фот. 2. Структура перелома (SEM) керама β-Al₂O₃ после исследований ионной проводимости

 $a - \times 600$, $b - \times 1800$



Phot. Fractures of β -Al $_2$ O $_3$ cerams (SEM) obtained by metasomatic re-sintering of α -Al $_2$ O $_3$ — sample $A, \times 1000, b$ — sample $B, \times 1000, c$ — sample $A, \times 3000, d$ — sample $B, \times 3000$

Andrzej SZYMAŃSKI, Władysław WOŁOSIŃSKI — The transformation of the phase composition of polycrystalline ceramic materials during metasomatic re-sintering





Phot. 2. Fracture of $\beta\text{-Al}_2\text{O}_3$ ceram after measurements of ionic conductivity a - \times 600, b - \times 1800