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ANDRZEJ PAWŁOWSKI*, ZBIGNIEW PĘDZICH**, MIROSŁAW M. BUĆKO**

DIFFUSION INDUCED GRAIN BOUNDARY MIGRATION (DIGM) PROCESS IN ZrO_2–Y_2O_3–MgO ION CONDUCTORS

PROCES DYFUZYJNIE WYMUSZONEJ MIGRACJI GRANIC MIĘDZYZIARNOWYCH (DIGM) W PRZEWODNIKACH JONOWYCH Z UKŁADU ZrO_2–Y_2O_3–MgO

Paper contains results of microstructure and chemical composition analyses of micrograins formed on initial grain boundaries in three systems: ZrO_2 + 6 mol. % Y_2O_3, ZrO_2 + 6 mol. % Y_2O_3 + 5.4 mol. % MgO and ZrO_2 + 6 mol. % Y_2O_3 + 12 mol. % MgO. It was found out that the micrograins appeared in the process of diffusion induced grain boundary migration (DIGM). They revealed an increased level of Y_2O_3 content (up to 2 mol. %) and a cubic symmetry. DIGM investigations were conducted after a heat-treatment of the samples at 1500°C for 50 hours and at 1700°C for 2 hours. Zirconia — yttria solid solution with magnesia particle addition showed the increase of amount of migration nuclei and the size of new-created grains. However, no change in the chemical composition of the grains was detected.

The mechanical properties and ion conductivity of the material were investigated. It was established that the ZrO_2 + 6 mol. % Y_2O_3 ceramic heat-treated at 1500°C showed the highest grain boundary conductivity. In investigated system the ratio (σ_{gb}/σ_{tot}) increases with the magnesia additive amount. This material has high hardness and slightly decreased fracture toughness. It seems to be a perspective material for solid electrolytes.

W pracy poddano analizie mikrostrukturę i skład powstających na granicach wyjściowych mikroziaren w tworzywach: ZrO_2 + 6% mol. Y_2O_3, ZrO_2 + 6% mol. Y_2O_3 + 5.4 % mol. MgO oraz ZrO_2 + 6% mol. Y_2O_3 + 12% mol. MgO. Stwierdzono, że powstały one w procesie dyfuzyjnie wymuszonej migracji granic międzyziarnowych (DIGM). Mikroziarna będące strefami dyfuzyjnymi posiadają podwyższoną zawartość o około 2% molowych Y_2O_3 i symetrię regularną. Badania procesu DIGM prowadzono po wygrzewaniu spieków w temperaturach 1500°C przez 50 godzin i 1700°C przez 2 godziny. Dodatek MgO w postaci cząstek do roztworu stałego powoduje zwiększenie ilości zarodków migracji na granicach i wielkości powstałych mikroziaren, nie zmienia natomiast ich składu.

* INSTYTUT METALURGII I INŻYNIERII MATERIAŁOWEJ IM. ALEKSANDRA KRUPKOWSKIEGO PAN, 30-059 KRAKÓW, UL. REYMONTA 25

** WYDZIAŁ INŻYNIERII MATERIAŁOWEJ I CERAMIKI, AKADEMIA GÓRNICZO-HUTNICZA, 30-059 KRAKÓW, AL. MICKIEWICZA 30

Badano właściwości mechaniczne i przewodnictwo jonowe tworzyw. Ustalono, że ceramika $ZrO_2+6\%$ mol. Y_2O_3 wyżarzana w 1500°C posiada najwyższe przewodnictwo jonowe po granicach ziaren, natomiast stosunek $(\sigma_{gb}/\sigma_{tot})$ rośnie wraz z dodatkiem MgO. Ceramika ta wykazuje podwyższoną twardość i nieznacznie obniżoną odporność na kruche pękanie. Tworzywo to może stanowić dobry materiał na elektrolity stałe.

1. Introduction

The process of diffusion induced grain boundary migration (DIGM) occurs in metal alloys [1, 2] and also in ceramic materials [3]. It process leads to formation of micrograins in the vicinity of grain boundaries as well as to step-like changes of chemical composition and grain orientation. These phenomena cause changes of physical and mechanical properties of materials.

The DIGM process in the ZrO_2–Y_2O_3 system usually induced the formation of narrow (200—300 nm) layers near the boundaries of primary grains (about 1 μm diameter) or wide grains, few micrometers in size, adjacent to big (20—30 μm) starting grains [4].

In the ZrO_2+6 mol. % Y_2O_3 system, the boundary migration in the DIGM process is connected with a rapid change of chemical composition at the front of reaction as well as a change of grain orientation. It brings about higher ion conductivity of materials [5]. J e o n g et al. [6] observed that the MgO addition aids the DIGM process in the mentioned system. P a w ł o w s k i et al. [5] revealed that MgO particles act as new starting points of grain boundary migration. In the presence of magnesia, the DIGM distance increases. Contrary to the Y_2O_3 contribution, the concentration of the MgO does not change in the material.

In the present paper, the formation of micrograins due to the grain boundary migration was described. The cell-structure was detected by the chemical composition investigations of a migration area in the ZrO_2–Y_2O_3–MgO system. In the examined system, the DIGM process influences the mechanical and electrical (especially ion conductivity) properties of the material by changes of its chemical composition and structure. The latter one is substantial for the material designed to be solid electrolyte.

2. Experimental

The materials used were solid solution powders of ZrO_2 with 6 mol. % Y_2O_3 produced by coprecipitation — calcination technique described in [7]. The materials containing magnesium were obtained by mixing of the zirconia and MgO powders in dry ethyl alcohol. In this way three materials were obtained: No. 1 — ZrO_2+6 mol. % Y_2O_3; No. 2 — ZrO_2+6 mol. % $Y_2O_3+5.4$ mol. % MgO and No. 3 — ZrO_2+6 mol. % Y_2O_3+12 mol. % MgO.

The powders were pressed uniaxially at 50 MPa and then isostatically at 350 MPa. Discs of 10 mm in diameter and 2 mm thick were sintered in air in a furnace with Superkanthal heating elements at 1500°C for 50 hour soaking time. The material No. 3 (ZrO_2+6 mol. % Y_2O_3+12 mol. % MgO) was also sintered at 1700°C for 2 hours producing the sample No. 4.

Microstructure observations were conducted using Philips XL 30 scanning electron microscope. The chemical composition was determined with EDS method using Oxford Instruments equipment (Link ISIS). Quantitative chemical analyses were conducted in areas ranged from 1 to 100 micrometers in diameter.

Ion conductivity measurements were performed with HP 34401A multimeter using d.c. four-probe and a.c. impedance spectroscopy methods. These techniques allow us to measure the grain boundary (σ_{gb}), bulk (σ_b) as well as the total (σ_{tot}) conductivities.

Hardness (HV) and fracture toughness (K_{Ic}) of the sintered samples were determined using Vickers indentation methods.

3. Results

3.1. Microstructure (SEM and TEM) and chemical composition (EDS) analyses

Fig. 1a shows the SEM micrograph of ZrO_2 with 6 mol. % Y_2O_3 heat-treated at 1500°C for 50 h (material No. 1), in which grains of about 20 μm are visible. The SEM/EDS measurements (Fig. 1b) reveal step increase of the yttria content in the boundary migration area up to 8 mol. % compared with 6 mol. % inside the grain. The *X*-ray diffraction measurements [4] showed the increase of amount of cubic zirconia phase in the material with the DIGM effect. The boundary migration was detectable in transmission electron microscope for a distance of about 600 nm (Fig. 2a). The EDS analysis showed in Fig. 2b revealed increase of the yttria content from 6.1 mol. % up to 7.6 mol. % in the migration zone.

The magnesia addition of 5.4 mol. % (material No. 2) induces grain boundary migration for the distance of 5 μm (Fig. 3a). Grains of MgO could be noticed at the primary grain boundaries. The EDS analyses show increase of the yttria content from 6 mol. % up to 7.6 mol. % (Fig. 3b) and slight decrease of magnesia content from 5.6 mol. % to 5.2 mol. % (Fig. 3c) in the migration zone. The stepwise change of chemical composition in newly created micrograins of about 5 μm proves the occurrence of the DIGM process in the migration area.

In material No. 3 which contains 12 mol. % of magnesia, grain boundaries migrate also in the distance of about 5 μm, whereas the starting grains are of about 10—20 μm (Fig. 4a). The chemical composition analyses in the migration area show the step change of yttria content up to 8 mol. %. The magnesia concentration changes from 6.8 mol. % to 7.5 mol. % (Fig. 4b, c). The observations of the DIGM process in

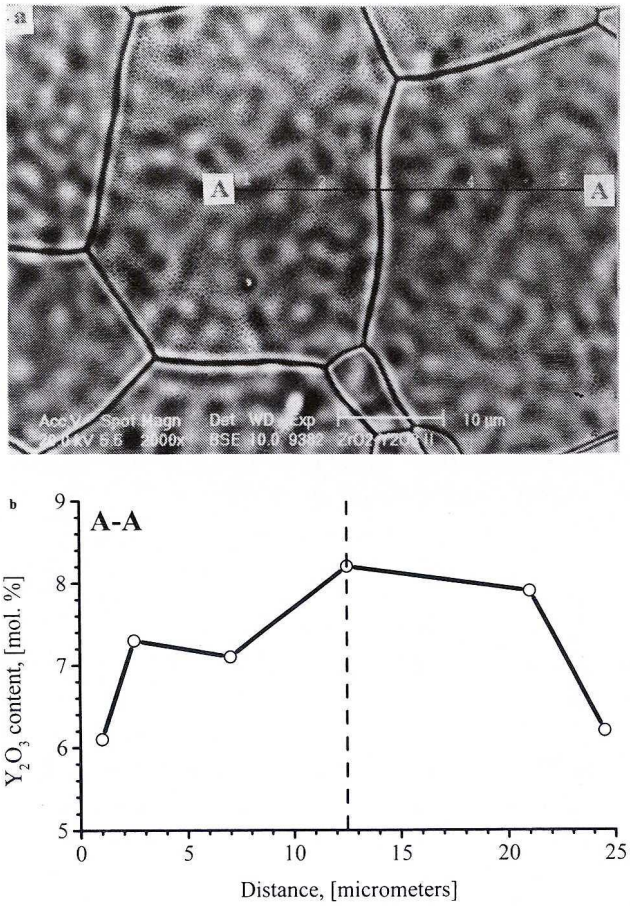

Fig. 1. SEM micrograph of the material: a — No. 1, ZrO_2 + 6 mol. % Y_2O_3 (1500°C/50 h), b — EDS analysis of Y_2O_3 at A–A cross-section

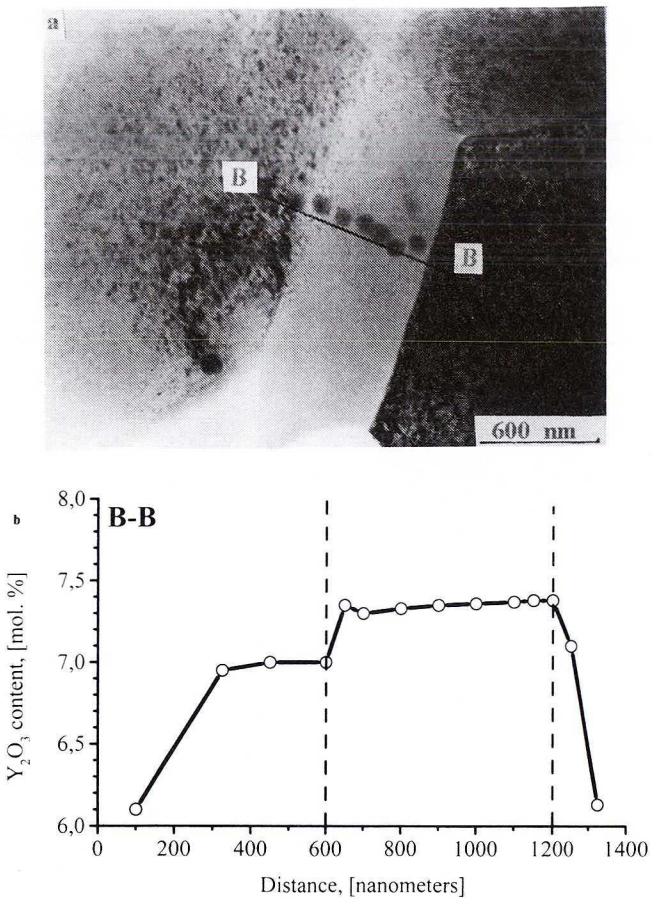

Fig. 2. TEM micrograph of the material: a — No. 1, ZrO_2+6 mol. % Y_2O_3 (1500°C/50 h), b — EDS analysis of Y_2O_3 at B–B cross-section

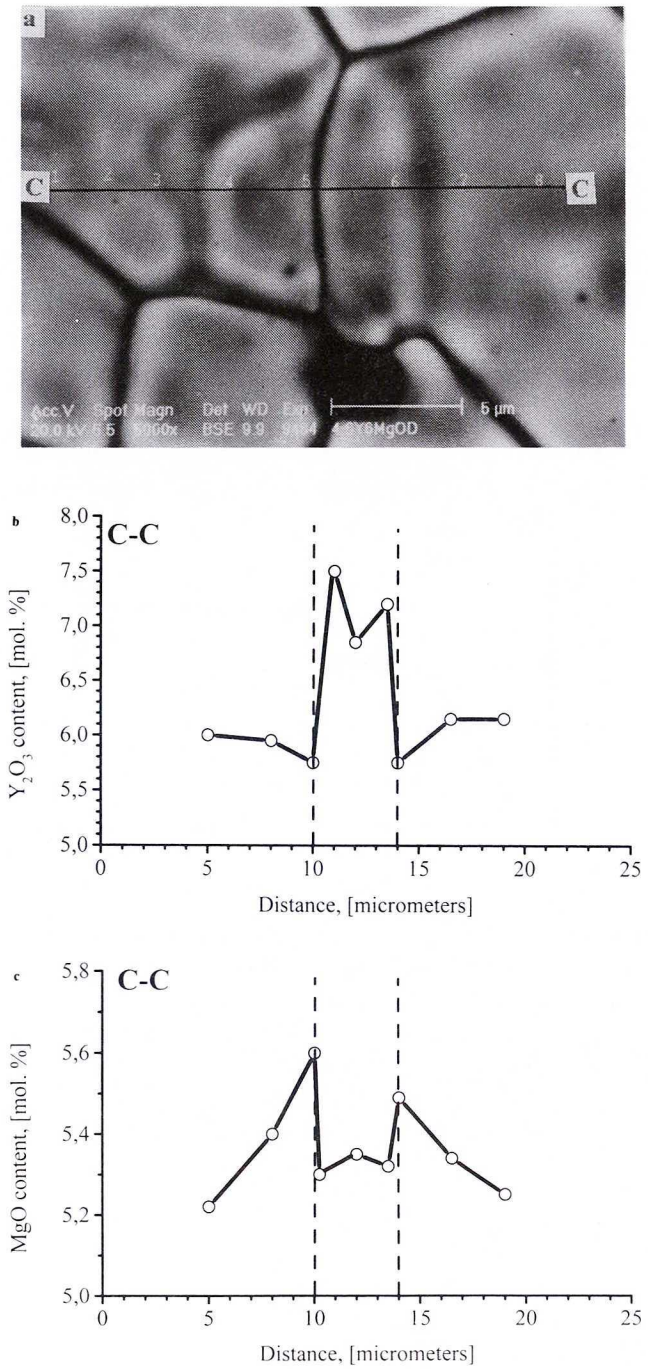

Fig. 3. SEM micrograph of the material: a — No. 2, ZrO_2+6 mol. % $Y_2O_3+5.4$ mol. % MgO (1500°C/50 h), b — EDS analysis of Y_2O_3 at C–C cross-section, c — EDS analysis of MgO at C–C cross-section

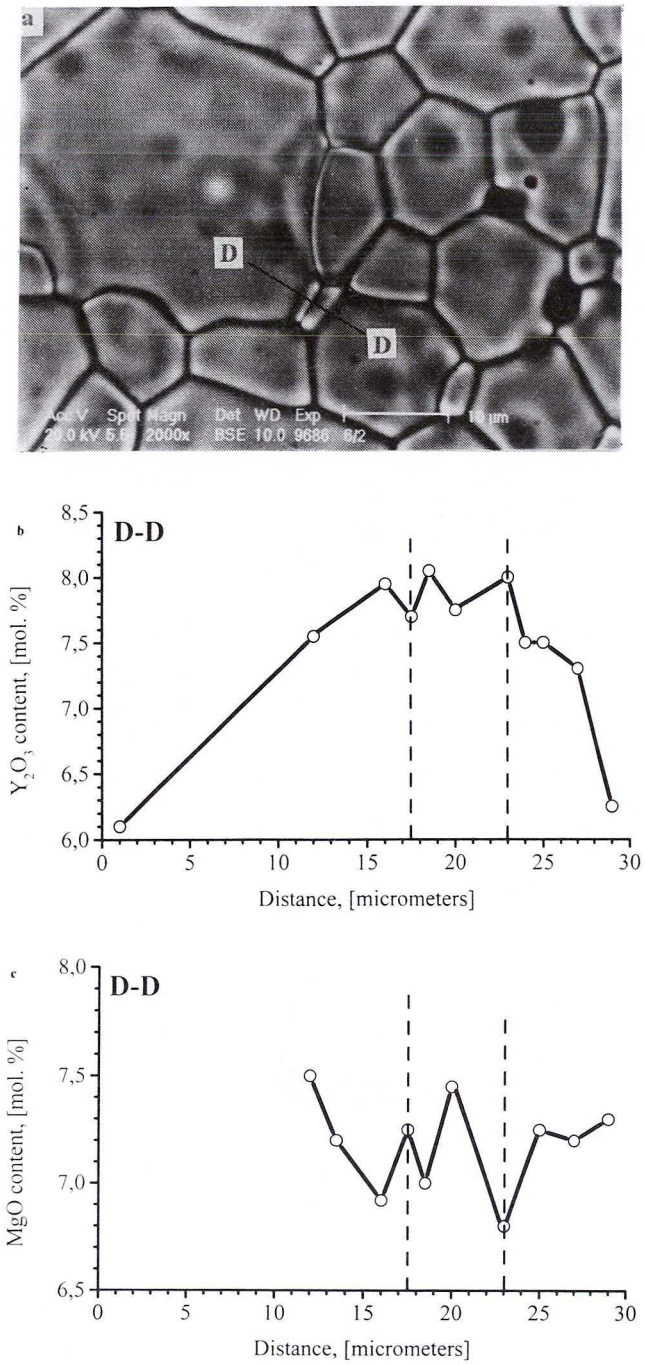

Fig. 4. SEM micrograph of the material: a — No. 3, ZrO_2+6 mol. % Y_2O_3+12 mol. % MgO (1500°C/50 h), b — EDS analysis of Y_2O_3 at D–D cross-section, c — EDS analysis of MgO at D–D cross-section

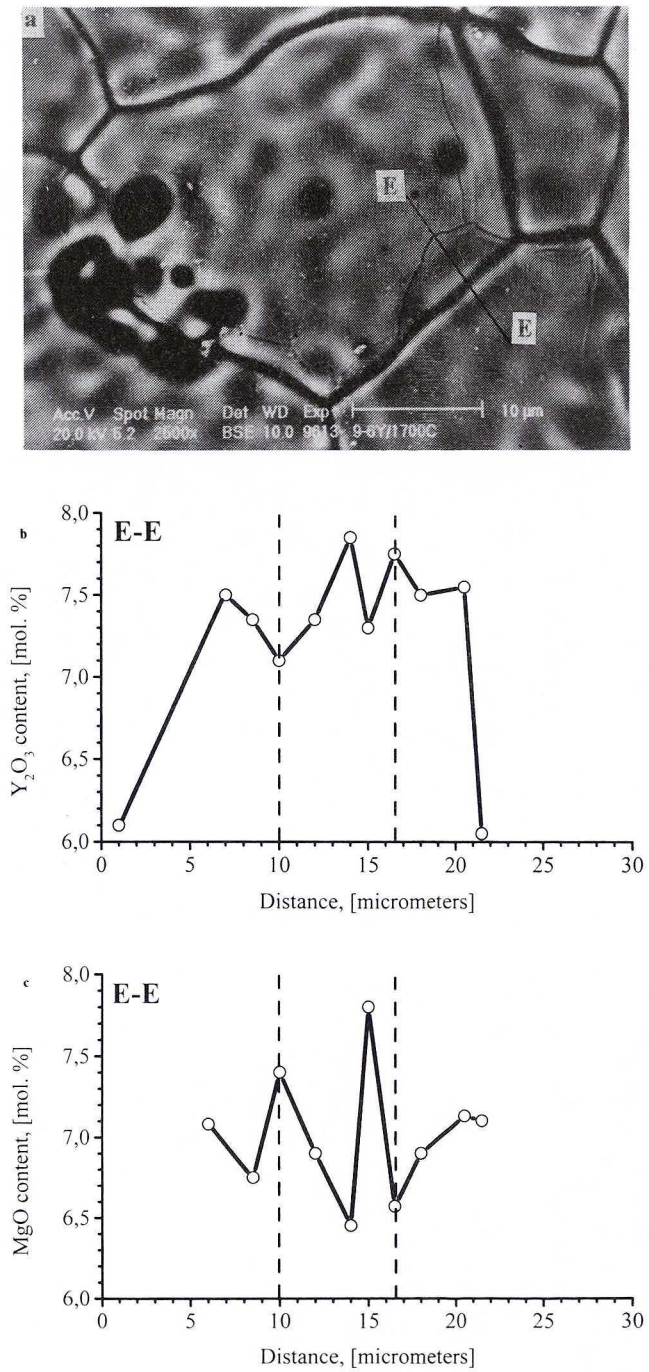

Fig. 5. SEM micrograph of the material: a — No. 4, ZrO_2+6 mol. % Y_2O_3+12 mol. % MgO (1500°C/50 h), (1700°C/2 h), b — EDS analysis of Y_2O_3 at E–E cross-section, c — EDS analysis of MgO at E–E cross-section

material No. 4 (ZrO_2 + 6 mol. % Y_2O_3 + 12 mol. % MgO, heat-treated at 1700°C for 2 h) show that the diffusion zones ranges up to 10 μm (Fig. 5a). The number of the migrating boundaries is much higher than in material No. 3 (heat-treated at 1500°C). The number of non-dissolved MgO particles is higher in material No. 4. The yttria concentration in the diffusion zones increases from 6 up to 7.9 mol. % (Fig. 5b). Magnesia content decreases from 7.4 to 6.4 mol. % (Fig. 5c).

The presented data suggest, that MgO addition induces the increase of number of migrating boundaries. The yttria concentration difference between diffusion zone and grain stays the same (about 2 mol. % Y_2O_3).

3.2. Conductivity measurements

The four-probe measurement results drawn in the Arrhenius co-ordinates reveal two temperature ranges of the conductivity (Fig. 6). The grain boundary conductivity dominates below 440°C, while, above 440°C, the bulk conductivity prevails. The linear form of the measured data allows us to calculate the activation energies of two mechanisms. Table 1 shows the activation energy and conductivity of the investigated materials for temperatures 400 and 600°C chosen from the two mentioned ranges. The bulk conductivity values obtained are similar to the results received by Bućko and Pyda [8].

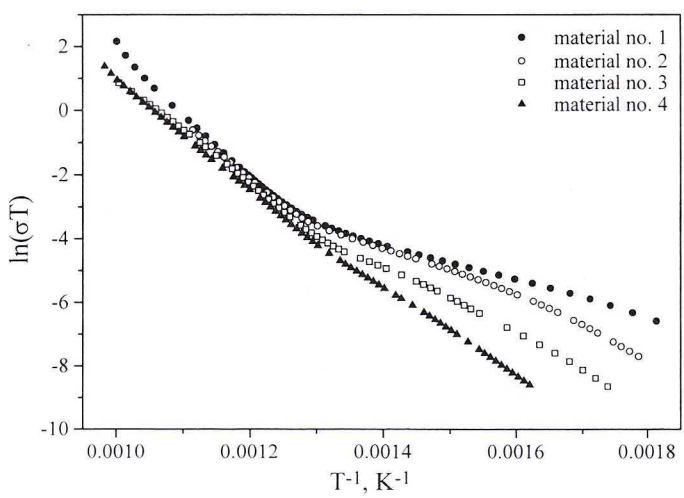

Fig. 6. Impendance spectroscopy diagrams for: a — No. 1, ZrO_2 + 6 mol. % Y_2O_3 (1500°C/50 h), b — No. 2, ZrO_2 + 6 mol. % Y_2O_3 + 5.4 mol. % MgO (1500°C/50 h), c — No. 3, ZrO_2 + 6 mol. % Y_2O_3 + 12 mol. % (1500°C/50 h), d — No. 4, ZrO_2 + 6 mol. % Y_2O_3 + 5.4 mol. % MgO (1700°C/2 h)

Fig. 6 shows that grain boundaries conductivities are the highest in material No. 1 and the lowest in material No. 4. The difference is two orders of magnitude in the temperature range of 300—400°C. In each case the magnesia addition decreases the ion conductivity of the material.

TABLE 1

Conductivities and respective activation energies of investigated materials

Material	σ, $(\Omega \cdot cm)^{-1}$		E_a, kJ/mol	
	400°C	600°C	grain boundary	bulk
1	$1.36 \cdot 10^{-5}$	$4.51 \cdot 10^{-4}$	48.0	159.5
2	$1.15 \cdot 10^{-5}$	$3.43 \cdot 10^{-4}$	68.9	133.7
3	$5.24 \cdot 10^{-6}$	$2.80 \cdot 10^{-4}$	88.7	136.1
4	$1.90 \cdot 10^{-6}$	$2.64 \cdot 10^{-4}$	113.5	143.2

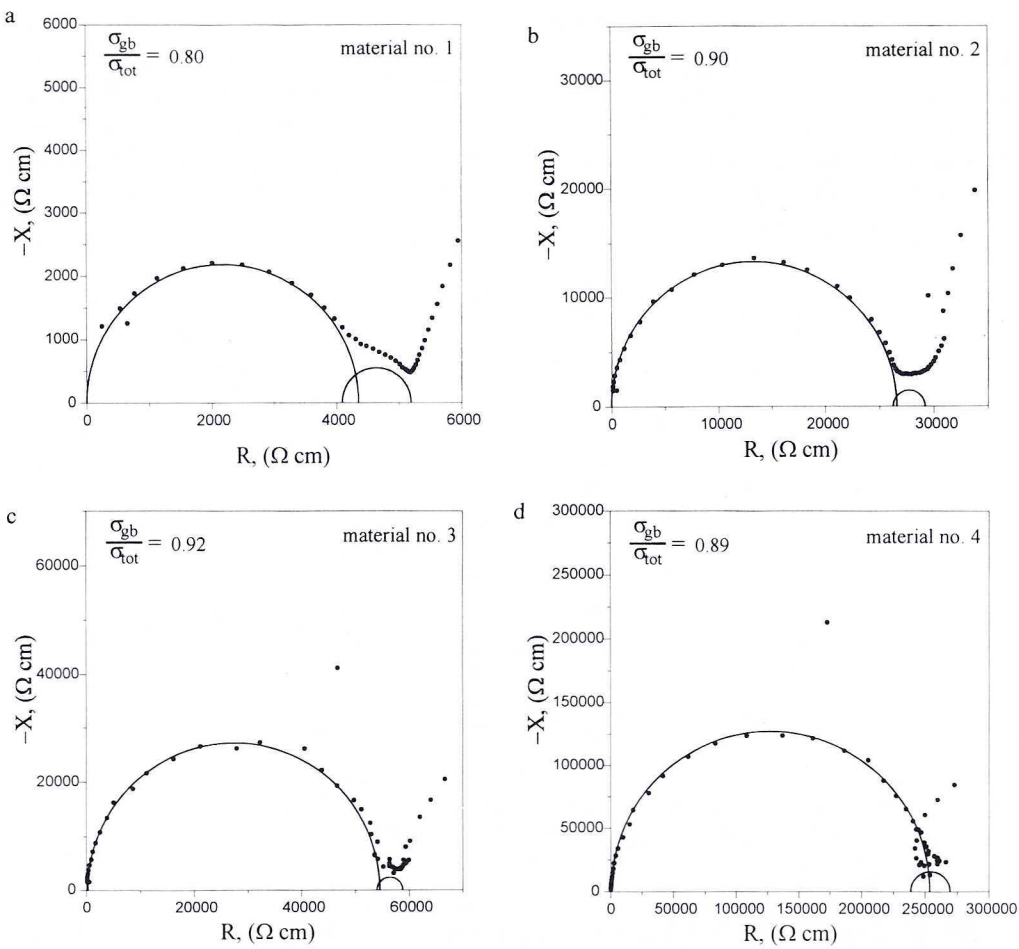

Fig. 7. Ion conductivity as a function of temperature: a — No. 1, $ZrO_2 + 6$ mol. % Y_2O_3 (1500°C/50 h), b — No. 2, $ZrO_2 + 6$ mol. % $Y_2O_3 + 5.4$ mol. % MgO (1500°C/50 h), c — No. 3, $ZrO_2 + 6$ mol. % $Y_2O_3 + 12$ mol. % MgO (1500°C/50 h), d — No. 4, $ZrO_2 + 6$ mol. % $Y_2O_3 + 5.4$ mol. % MgO (1700°C/2 h)

Figures 7a-d show the impedance spectroscopy diagrams measured at 500°C for all the tested materials. These diagrams could be approached with two semicircles and a straight line due to grain boundary (σ_{gb}), bulk (σ_b) and electrode conductivities, respectively. The grain boundary conductivity to the total one (σ_{tot}) ratio increases with the magnesia content in the zirconia-yttria solid solution. For material No. 1 (ZrO_2+6 mol. % Y_2O_3, 1500°C/50 h) $\sigma_{gb}/\sigma_{tot} = 0.80$. The sample No. 2 ($ZrO_2+6$ mol. % $Y_2O_3+5.4$ mol. % MgO, 1500°C/50 h) has $\sigma_{gb}/\sigma_{tot} = 0.90$ and material No. 3 (ZrO_2+6 mol. % Y_2O_3 +12 mol % MgO, 1500°C/50 h) reveals $\sigma_{gb}/\sigma_{tot} = 0.92$. Material No. 4 ($ZrO_2+6$ mol. % Y_2O_3+12 mol % MgO, 1700°C/2 h) has a similar value of $\sigma_{gb}/\sigma_{tot} = 0.89$.

These data indicate that the grain boundary conductivity contribution to the total one increases with the magnesia content. However, the growth of newly created grains in the grain boundary migration zone decreases the total ion conductivity.

3.3. Mechanical properties measurements

Table 2 shows the Vickers hardness (HV) and fracture toughness (K_{Ic}) of the studied materials. They decrease slightly with the increase of the magnesia content. The microstructural observations show that this is due to widening of the grain boundary migration zone in DIGM process. The changes of the mechanical properties could be caused by increase of the amount of cubic zirconia solid solution after the DIGM. Non-dissolved magnesia particles located at the primary grain boundaries could also play a role in the process.

TABLE 2

Hardness and fracture toughness of investigated materials

Material	Vickers Hardness HV, [GPa]	Fracture Toughness K_{Ic}, [MPa·m$^{0.5}$]
1	13.8±0.7	3.1±0.4
2	13.3±0.3	2.7±0.5
3	13.5±0.2	2.6±0.5
4	13.2±0.5	2.4±0.7

4. Conclusions

The chages of chemical composition and microstructure of the analysed materials allow us to state that during the heat-treatment at 1500°C for 50 h the grain boundary migration was induced resulting in appearance of new micrograins. They have cubic crystallographic symmetry [4], contrary to the primary grains where tetragonal and cubic symmetries were detected. The newly created micrograins show

stepwise chemical composition changes at the migrating boundary. This confirms a non-linear mechanism of their formation, which is characteristic for the DIGM. This process takes place in material No. 1 ($ZrO_2 + 6$ mol. % Y_2O_3, 1500°C/50 h) for the distance of 600 nm and it causes increase of yttria concentration in the migration zone up to 2 mol. %. In material No. 2 ($ZrO_2 + 6$ mol. % $Y_2O_3 + 5.4$ mol. % MgO, 1500°C/50 h) the yttria concentration increase in migration zone also reaches 2 mol. % but the width of grain boundary zone (due to coarsening of micrograins) increases up to 10 μm. Almost all primary grain boundaries show tendency to migration.

The diffusion induced grain boundary migration was detected in all investigated materials. In material No. 1 DIGM occurred for the distance of 600 nm, in materials No. 2 and 3 for 5 μm and for 10 μm in material No. 4. The yttria concentration in the migration zone in each case reached about 8 mol. % giving rise to the amount of the phase with cubic symmetry. In materials containing MgO, some part of magnesia was present in the solid solution, and the rest at the primary grain boundaries. The MgO content lowered to 5.2 mol. % in the new micrograins. For material No. 2, the total amount of $Y_2O_3 + MgO$ was about 12 mol. %. For material No. 3 and 4 the total amount of $Y_2O_3 + MgO$ in the migration zone is 14.5 mol. %. The balance of about 3 mol. % was found at the starting grain boundaries.

The presented changes of microstructure and chemical composition, due to the magnesia addition, result in increase of the σ_{gb}/σ_{tot} ratio from 0.80 up to 0.92. This confirms the DIGM process to be activated. When the level of magnesia addition is high (12 mol. %) the growth of new grains is responsible for the decrease of ion conductivity of the material by two orders of magnitude. The highest grain boundary conductivity shows material No. 1 (see Tab. 1) heat-treated at 1500°C for 50 h which is slightly more than the conductivity of the same material heat-treated at 1700°C for 2 h [5].

To sum up, the DIGM effect in the zirconia — yttria solid solution with magnesia addition (from 5.4 to 12 mol. %) causes a cell-like material microstructure with newly created micrograins adjacent to the primary grain boundaries. These micrograins have increased yttria content and cubic symmetry. Such a microstructure accounts for high grain boundary conductivity, but is a reason for the decrease of the bulk conductivity. As regards electrical and mechanical properties these materials could be used as of solid electrolytes.

Acknowledgements

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REVIEWED BY: DOC. DR HAB. INŻ. BOGUSŁAW MAJOR

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