Electrochemical characterisation of 3Y-TZP–Fe₂O₃ composites

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Abstract

The influence of the addition of ferric oxide to 3Y-TZP on the conductivity and microstructure of sintered Y-stabilised tetragonal zirconia ceramics (3Y-TZP) was investigated. A comparison was made between two different dense 3Y-TZP– α -Fe₂O₃ composites. Compacts were made by pressureless sintering at 1150 °C or by sinterforging at 1000 °C and 100 MPa. The sinterforging process resulted in smaller zirconia and hematite grains and a higher monoclinic zirconia content as compared to the compact that was sintered pressureless. The high monoclinic content led to loss of ionic conductivity. The addition of ferric oxide caused electronic conductivity. The sinterforging resulted in a high concentration of metastable defects in the zirconia–hematite composite, leading to a relatively high electronic conductivity. Heating above 380 °C caused irreversible loss of these defects and a large decrease in electronic conductivity.

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1. Introduction

It is well known that the electronic and/or ionic conductivity of oxides can change significantly with grain size. For example, the electronic conductivity of a dense CeO_{2–x} compact with average grain size of 10 nm was reported to be a factor 10⁴ higher than for a coarse-grained CeO_{2–x} compact [1]. For 3 mol%

Y₂O₃-doped tetragonal zirconia polycrystals (3Y-TZP) the ionic conductivity normally decreases with grain size, due to a blocking effect of the grain boundaries [2]. Studies of the ionic conductivity of yttria-doped zirconia were focused mainly on the influence of yttria content [3,4] and of grain boundaries [2,5]. The latter increases with decreasing grain size. To date, only one report exists on the conductivity of yttria-doped zirconia with grains in the nano-range (<100 nm), where grain boundaries showed enhanced specific conductivity due to a lower than usual concentration of Si at the grain boundaries [6]. The distribution of (second) phases in the material has also been shown to affect conductivity [7].

Addition of Fe₂O₃ to yttria-doped zirconia can induce electronic conductivity in the materials, which

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strongly increased with the added amount of dissolved iron oxide. The activation energy of electronic conductivity decreased with the amount of iron oxide added [8–11]. In some cases, the amount of second phase hematite seemed to have no influence on the conduction behaviour [9,10], but it has also been reported that with increasing amounts of second phase grain boundary conductivity slowly decreased [11]. The nature of the different types of conduction in hematite is not well understood. The conduction has been tentatively attributed to electrons, but also to cation excess and cation vacancies [12]. In general, it appears that results and interpretations presented in the literature are rather contradictory. This can partly be ascribed to different microstructures (grain size homogeneity, etc.).

In this study, the influence on conductivity and microstructure of ferric oxide addition to fine-grained 3Y-TZP has been investigated. Two types of zirconia- α -Fe₂O₃ composites are compared, a pressureless sintered compact and a composite prepared by sinterforging. The latter samples presented a significantly smaller grain size. A 3Y-TZP compact was made in the same way as the large-grained zirconia-hematite composite in order to study the influence of hematite on the material properties. A comparison between the two zirconia-hematite composites reveals the influence of the microstructure on the electrical properties.

2. Experimental

2.1. Synthesis of materials

The preparation of the compacts has been described previously [13,14]. An aqueous solution of FeCl₃ 6H₂O (Fluka) was added to a suspension of 3Y-TZP. By raising the pH of the mixture, the ferric ions were subsequently precipitated. The (partly) amorphous gel was washed with water to remove any water-soluble species and subsequently, with ethanol to remove water. After drying at 100 °C, the gel was ground in a mortar and calcined in air for 2 h at 500 °C (heating rate of 2 °C/min) [13]. The powders were pre-pressed isostatically at 200 MPa, followed by isostatic pressing at 400 MPa resulting in cylindrical samples with dimen-

sions of approximately 8 mm length and 6 mm diameter.

A green compact was pressureless sintered at 1150 °C for 2 h in air (heating at 2 °C/min, cooling at 4 °C/min) (sample code S1150). Another sample was sinterforged at 1000 °C (sample code SF1000). SF1000 compacts were first pre-sintered for 2 h at 900 °C. The resulting compact was placed between SiC pistons and sinterforged using the following process program [13]:

- heating with 10 °C/min to a pre-sinter temperature of 900 °C
- heating with 2 °C/min up to 950 °C, 50 °C below the final sinterforging temperature
- heating further with 2 °C/min to the final temperature of 1000 °C, while at the same time increasing the pressure from 0 to a final pressure of 100 MPa
- holding time of 25 min
- release of pressure and cool down to room temperature.

2.2. Microstructural characterisation of the materials

The chemical composition of the powder was determined with quantitative X-ray-fluorescence spectrometry (XRF) using a Philips PW 1480/10-fluorometer, as described in Ref. [15]. The phase composition of the compacts was investigated with a Philips X'Pert-1 PW3710 XRD diffractometer using Cu K α

Fig. 1. Schematic representation of the measurement set-up. R_M is the reference resistance. The differential amplifier outputs are connected to channels 1 and 2 of the FRA. The data is corrected for the parasitic capacitances C_M and C_s .

Table 1
Phase composition and microstructure of the investigated compacts

Material	Hematite (vol.%)	$T_{\text{sint.}}$ (°C)	$P_{\text{sint.}}$ (MPa)	Zirconia d_{grain} (nm)	Hematite d_{grain} (nm)	Relative density (%)	t-ZrO ₂ / total ZrO ₂ (%)
3Y-TZP	0	1150	0	122		97	97
3Y-TZP– α -Fe ₂ O ₃	20	1150	0	110	183	96	71
3Y-TZP– α -Fe ₂ O ₃	20	1000	100	80	84	94	25

radiation. The tetragonal/monoclinic zirconia ratio was determined using the calibration curve of Toraya et al. [16].

Compact densities were determined using the Archimedes technique in water. The microstructure of the compacts was investigated with scanning electron microscopy (SEM). For the pressureless sintered compacts, a Philips XL30 Environmental Scanning Electron Microscope–Field Emission Gun (ESEM-FEG) was used to produce the backscatter electron (BSE) and secondary electron (SE) images at different magnifications. The sinterforged-compact was investigated with a Hitachi S4700. The micrographs were used to determine the average grain size of the grains

of both the zirconia and hematite phase. The average grain sizes of the two phases were calculated using the lineal intercept method [17].

2.3. Impedance measurements

The electrochemical impedance was measured in a two-electrode geometry. Gold electrodes were deposited on both polished surfaces of the sample using a dc sputtering apparatus. The frequency dispersion was measured with either a Solartron 1250 or a Solartron 1255 Frequency Response Analyser (FRA). The FRA was operated under control of a ‘Personal Computer.’ A homemade dual differential

Fig. 2. BSE- (left) and SE-images (right) of the pressureless sintered (A, B) and the sinterforged (C, D) 3Y-TZP– α -Fe₂O₃ dual-phase composites. The dark areas in the BSE-images represent the hematite grains.

amplifier was used in order to increase the input impedance of the FRA system (which is typically 1 M Ω at low frequencies). The schematic arrangement is presented in Fig. 1. The measured impedances were corrected for the parasitic cable capacitances (about 100 pF).

In order to facilitate the distinction between bulk and electrode processes, the dispersions were measured on sets of two samples with near-identical cross-sections but with different thicknesses. The thickness ratio of the thick to thin sample (respectively denoted as ‘large’ and ‘small’) was 5:1. Gold electrodes were used as these show little catalytic activity with respect

to the dissociation of ambient oxygen. Hence, these electrodes can be regarded as ‘ionically blocking’ electrodes.

The thick and thin samples were placed together between solid gold electrodes in the high-temperature measurement cell, using a common, central gold electrode. A flow of 80% N₂/20% O₂ at 100 cm³/min (STP) was used as ambient.

The validity of the data was tested with a Kramers–Kronig transformation compatibility test program [18]. Data analysis was performed with the ‘complex nonlinear least squares fit’ (CNLS) software package ‘Equivalent Circuit’ [19–21].

Fig. 3. Impedance representation of the frequency dispersion of 3Y-TZP– α -Fe₂O₃ dual-phase composite S1150 samples at 221 °C. The high-frequency part is enlarged in the insets. (O) Measured data, (—■—) CNLS-fit.

3. Results

3.1. Composition and microstructure of the compacts

The elemental analysis indicated that the composite consists of 27 mol% $\text{FeO}_{1.5}$ and 73 mol% 3Y-TZP. The microstructural parameters of the investigated compacts are given in Table 1. The density of the three compacts was $\geq 94\%$. The volume percentage of hematite phase in the composites is estimated at 20% assuming that approximately 2 mol% Fe_2O_3 remains dissolved in the 3Y-TZP lattice after sintering [5]. For a homogeneously distributed system, this volume percentage is below the percolation threshold.

XRD-analysis showed that in the sinterforged zirconia–hematite composite, the majority (75%) of the zirconia had the monoclinic structure. The average zirconia grain sizes of the pressureless sintered 3Y-TZP compact (122 nm) and the 3Y-TZP– $\alpha\text{-Fe}_2\text{O}_3$ composite (110 nm) are almost equal. The average grain sizes of the hematite and zirconia grains of the sinterforged composite were both < 100 nm. In Fig. 2 the microstructures of the pressureless sintered (S1150) and sinterforged (SF1000) compacts are pre-

Table 2

Activation energies and pre-exponential factors for the total and grain-bulk ionic conductivity of the pressureless sintered S1150 sample

Conductivity	σ_0 , (S K cm^{-1})	E_{act} , (kJ mol^{-1})
σ_{tot} (small)	2.5×10^5	101
σ_{tot} (large)	2.9×10^5	101
σ_{ion} (average)	3×10^5	85

sented. The dark areas in the backscattered (BSE) images represent the hematite phase. These images clearly indicate that the hematite phase is not percolative. The SE-images have been used for the determination of the average grain sizes.

3.2. Analysis of the electrical properties of the S1150 samples

In Fig. 3, the low-temperature (221 °C) impedance curves are presented for the S1150 samples. The frequency dispersion is dominated by a very large depressed semicircle, which represents the grain boundary resistance. The corresponding parallel capacitance value of ~ 2 nF, calculated for the maximum of this semicircle, can be considered typical for grain boundary dispersion.

At the high-frequency side, a second small semicircle can be discerned. There is a very strong overlap between the two semicircles, as can be seen from the enlargements in the insets in Fig. 3. Due to this strong overlap, the CNLS analysis yields only approximate values for the high-frequency resistance, which represents the inverse ionic conductivity.

In the Arrhenius graph of Fig. 4, these ionic conductivity values are compared with results obtained for pure 3Y-TZP by Santos et al. [2]. A good agreement for both the thin (small) and the thick (large) sample is obtained. The ionic conductivity of the pressureless sintered pure 3Y-TZP sample (not shown) was identical to the results of Santos et al. [2]. Due to the small grains, this composition showed a clear grain boundary resistance, but significantly smaller than for the 3Y-TZP– $\alpha\text{-Fe}_2\text{O}_3$ samples.

The total ionic conductivity (grain bulk plus grain boundary) for the S1150 samples is also presented in Fig. 4. An almost exact agreement between the two different-sized samples is obtained. As the grain bulk

Fig. 4. Arrhenius plot of the total conductivity (closed symbols) and the ionic conductivity (open symbols) for the 3Y-TZP– $\alpha\text{-Fe}_2\text{O}_3$ dual-phase composite S1150. The heavy upper line represents the ionic conductivity of pure 3Y-TZP [2].

ionic resistance is quite small with respect to the grain boundary resistance, the total conductivity may be taken for the grain boundary ‘conductance.’ The corresponding pre-exponential factors and activation energies for the total conductivity are presented in Table 2. The activation energy and pre-exponential factor for the ionic conductivity is calculated for the combined set of data.

With increasing temperature, the electrode dispersion becomes visible. Despite the rather inactive gold electrodes, a dc electrode resistance can be observed, see the dispersions in Fig. 5 for the S1150 samples at 527 °C. The minimum in the dispersion represents the total ionic resistance.

At temperatures above 600 °C the electrode response shows a complicated structure (see Fig. 6).

CNLS-analysis of the data leads only to an acceptable result when a so-called ‘Gerischer element’ [22,23] is used in the electrode dispersion. The Gerischer impedance combines semi-infinite diffusion (Warburg) with a chemical side reaction. This results in a finite dc value of the Gerischer impedance. The non-Faradaic side reaction can easily be represented by an interaction between the oxygen concentration in the bulk 3Y-TZP phase and the (poorly) mixed conducting hematite phase. The implications will be analysed further in the Discussion.

Indications for some degree of electronic conductivity are obtained from a comparison of the electrode dispersions at high temperatures for the ‘small’ and the ‘large’ samples. The analysis shows that the resistive part of the electrode dispersion

Fig. 5. Impedance representation of the frequency dispersion of 3Y-TZP- α -Fe₂O₃ dual-phase composite S1150 samples at 527 °C. (O) Measured data, (—■—) CNLS-fit.

Fig. 6. Impedance representation of the frequency dispersions for the S1150 type samples at 681 °C. (O) Measurement, (—■—) CNLS-fit. The heavy line represents the separate contributions to the dispersion. The mid-frequency dispersion is modelled with a 'Fractal Gerischer' dispersive element.

scales with the geometric factor (thickness) of the samples. The dispersive part, i.e. the CPE-element is more or less independent of the geometric factor and hence, pertains to the electrolyte/electrode interface, as is also indicated by the magnitude of the CPE:

$$Q - Y_0 = 1 \times 10^{-5} - 4 \times 10^{-4} S s^n (n \approx 0.5).$$

In an alternative CNLS analysis, it was assumed that the extrapolated dc point represents a parallel electronic conductivity. In this analysis, the gold electrodes were regarded as ideal ionically blocking electrodes, i.e. having no finite dc electrode resistance. For $T > 600$ °C consistent results were obtained as can

be seen from the Arrhenius graph in Fig. 7. Both the total ionic and the thus obtained electronic conductivity scale with the sample thickness. This clearly indicates that both are bulk transport processes. The electrode dispersion (represented by a constant phase element, closely related to a Warburg, or diffusion type element) remains independent of sample thickness (Fig. 7, right-hand axis).

It can be seen clearly from Fig. 7 that the assumption of a parallel electronic conductivity is a viable alternative. The analysis, however, does not allow a definite statement to be made on the magnitude of the electronic conductivity. The presented values must be seen as an upper limit. The estimated activation energies and pre-exponential values are presented in Table 3.

Fig. 7. Arrhenius plot of the analysis of 3Y-TZP- α -Fe₂O₃ dual-phase composite S1150 samples assuming an electronic conductivity (lower line, open symbols) in parallel with the ionic conductivity (middle line, closed symbols). The electrode dispersion parameter is presented on the right-hand axis (upper line, closed triangles).

3.3. Analysis of the electrical properties of the SF1000 samples

The impedance measurements on the 3Y-TZP-hematite samples, sinterforged at 1000 °C (SF1000), were also performed on two samples with nearly identical cross-section but with different thickness. The impedance spectra indicate a quite different behaviour. The conductivity is clearly dominated by an electronic conduction, which is obvious from the absence of electrode dispersion. This is clearly demonstrated by the impedance diagrams of Fig. 8 (231 °C) and Fig. 9 (400 °C). The general equivalent circuit presented in Fig. 10 can be used to model the impedance dispersion for both specimens.

The CNLS-analysis indicates that the grain boundary resistance is most likely very large (see circuit in Fig. 10). It cannot be estimated with the CNLS procedure. The magnitude of the constant phase element (CPE or pseudo-capacitance), which presents the dispersive part of the grain boundary impedance, is in the same range as observed for the S1150 samples. It is clearly a bulk property as it scales quite well with the thickness of the samples, as is evident from Fig. 11.

The first set of measurements was started at 231 °C with increasing temperature. At around 360 °C, the measured impedance was no longer stable with time. This also becomes evident from the Arrhenius graph of the electronic conductivity and the ‘assumed’ ionic conductivity for both samples (Fig. 12). Unfortunately, the scatter in the data points for the thin sample (small) is quite large, but for the ‘large’ sample, a clearly activated conductivity is observed for both the electronic and ionic components. For comparison, the ionic conductivity of 3Y-TZP [2] is presented as well. Above 350 °C, the electronic conductivity starts to deviate from the Arrhenius behaviour, showing a relative decrease in conductivity with respect to the extrapolated value. Both samples show the same behaviour.

After the measurements at 434 °C, both samples were cooled down. A second measurement run with increasing temperature that was started at 126 °C. Data could be analysed again in terms of the equivalent circuit of Fig. 10. The electronic conductivity had decreased irreversibly, but still showed Arrhenius behaviour up to a temperature of 360 °C, as is evident from the Arrhenius graph of Fig. 13. The ‘ionic conductivity’ showed significantly more scatter, but could still be derived from the CNLS analysis. The estimated activation energy had decreased, however, from ~ 125 to ~ 75 kJ·mol⁻¹. This large change indicates that it is highly unlikely that this ‘high-frequency’ conductivity pertains to the ionic conductivity only. It is unfortunately not possible to elucidate the actual and possibly more complex mechanism that leads to this conductive process.

At 400 °C, both samples again showed a dispersion, which changed slowly with time. Therefore, the impedance was measured as a function of time over a period of 70 h. The electronic conductivity could be fitted to an exponential decay for both samples, see

Table 3

Activation energy and pre-exponential value for the ionic and electronic conductivity for the pressureless sintered sample S1150, assuming electronic bulk conductivity

Parameter	σ_0 , (S K cm ⁻¹)	E_{act} (kJ mol ⁻¹)
$\sigma_{tot, ion}$	1×10^5	96
σ_{el}	9×10^4	100
Q-Y ₀	1.5 (S s ⁿ)	72

The activation energy and pre-exponential value for the electrode dispersion (Warburg) is also presented.

Fig. 8. Impedance representation of the frequency dispersions for the SF1000 type samples at 231 °C. (O) Measured data, (—■—) CNLS-fit.

Fig. 14. The corresponding decay times, however, differed considerably for both samples. The decay time for the 'small' sample was less than that for the 'large' sample (14.4 vs. 22.2 h).

After the time relaxation experiment, the impedance was measured in a few steps up to 750 °C and left for some time at this temperature. A final run of impedance measurements was performed with decreasing temperature. For this set of measurements, the 'ionic or high-frequency conductivity' could not be established from the CNLS analysis. The corresponding resistances were too small with respect to the electronic resistances at all temperatures. The data was analysed with the simple equivalent circuit of Fig. 15. The electronic resistance showed Arrhenius behaviour over the entire temperature range. The conductivity data of this third

temperature run has also been presented in the combined Arrhenius graph of Fig. 13. It is remarkable that the conductivity values for both samples are quite close, while for measurement runs 1 and 2, a significant difference could be observed.

The estimated activation energies and pre-exponential factors have been compiled in Table 4 for comparison.

4. Discussion

4.1. The S1150 samples

One of the important issues is whether the composite shows electronic conductivity. The volume fraction

Fig. 9. Impedance representation of the frequency dispersions for the SF1000 type samples at 400 °C. (O) Measured data, (—■—) CNLS-fit.

of the hematite phase is below the percolation threshold. But it is unknown whether an Fe-enrichment may occur at the grain boundaries of the 3Y-TZP phase. The introduction of the hematite phase causes a considerable decrease in grain boundary conductivity (as compared to the influence of grain size only [2]). A strong indication for electronic conductivity is found in the analysis of the electrode dispersion. It may be contended that the electrode dispersion and apparent dc value is due to a porous electrode structure, but in that case, the electrode resistance should scale with the electrode surface area, i.e. it should be virtually the same for both the thick and the thin sample.

Furthermore, it is found that the ionic conductivity is more or less equal to the ionic conductivity of pure 3Y-TZP (see Fig. 4). One would expect a lower value for the composite, as the hematite part shows very poor oxygen ion conductivity and hence, does not contribute. On the other hand, assuming that the parallel electronic conductivity model is valid, this will automatically lead to a lower estimate for the ionic conductivity value.

Finally, the complicated electrode response for $T > 600$ °C, which is the observed Gerischer impedance response and the Warburg type low-frequency dispersions, indicate oxidation–reduction processes at

Fig. 10. Possible 'Equivalent Circuit' that can model the impedance spectra for the SF1000 type specimen. The elements, outlined by the broken lines, cannot be retrieved from the CNLS analysis.

the electrode interfaces coupled to 'Faradaic' bulk diffusion. For this process, it is essential that both ionic and electronic conductivity is present in the sample. The observed Gerischer impedance can only be explained by a diffusion process coupled to a chemical side reaction [22,23]. This side reaction can be envisioned to represent an equilibration between the ac-modulated oxygen activity in the 3Y-TZP phase and the (in principle) unaffected oxygen activity in the hematite phase.

Fig. 11. Magnitude of the CPE dispersion ascribed to the grain boundary impedance. The CPE, in admittance representation, is given by $Y_0(j\omega)^n$. n is typically around 0.75. Open symbols: relative to cross-section. Closed symbols: corrected for sample geometry.

Fig. 12. Arrhenius graph of the electronic and ionic conductivity for the SF1000 samples (first temperature run). The data of the 'large' sample have been fitted to an Arrhenius expression in the range 231–366°C. The ionic conductivity of 3Y-TZP (Ref. [2]) is included for comparison.

Fig. 13. Compilation of the electronic conductivity for the SF1000 samples for the three consecutive temperature runs. Numbers indicates runs, arrows indicate the direction of the measurement sequence.

Fig. 14. Relaxation of the electronic conductivity of the SF1000 samples at 400 °C. The lines represent the fitted exponential decay curves.

4.2. The SF1000 samples

Due to the complexity of these impedance spectra, it is very difficult to assign the observed circuit elements to specific conductive or resistive (blocking) processes. When the hematite phase is percolative, it will cause a (parallel) electronic conductivity. The typical activation energy for this conductivity in hematite under normal conditions ($pO_2 = 0.2$ bar) is

Fig. 15. Schematic representation of the simplified equivalent circuit, used in the CNLS analysis of the third temperature run.

Table 4

Activation energies for the (electronic) conductivity observed in the three subsequent runs of the sinterfired 3Y-TZP–hematite samples, SF1000

Sample	E_{act} , (kJ mol ⁻¹) Run-1	E_{act} , (kJ mol ⁻¹) Run-2	E_{act} , (kJ mol ⁻¹) Run-3
σ_{tot} (small)	75	84	113
σ_{tot} (large)	77	85	117
σ_{ion} (average) $\sim$ 125	—	—	—

about 90–110 kJ·mol⁻¹ (Ref. [12], see also the compilation of conductivities in the Arrhenius graph of Fig. 16). But besides a possible conduction through the hematite phase, there may also be an electronic path through the grain boundary layers of the 3Y-TZP phase. This may be either a separate and very thin phase, but it can well be a more electronically conducting region in the grain boundary area, due to segregation of the Fe-ions in the 3Y-TZP phase. The SF1000 samples have a much larger grain boundary surface than the S1150 samples. Hence, the increased electronic conductivity with respect to the S1150 samples can be easily explained in these terms.

Fig. 16. Summary of the total conductivities of the S1150 and SF1000 samples in an Arrhenius graph. For comparison, literature values are presented for related compounds. m-ZrO₂ is monoclinic zirconia [9]. m-ZrO₂–Fe₂O₃ is composite with composition: 0.9 (m-Zr_{0.905}Fe_{0.095}O_{1.953})^{-0.1} (α-Fe₂O₃) [9]. The broken line represents α-Fe₂O₃ [12].

In the CNLS-analysis of the first and second measurement runs, another conductive process could be indicated. This is tentatively ascribed to ionic conduction, but in the current situation, it is not possible to substantiate this. There is also a strong indication for a very large grain boundary resistance, which seriously impedes the ionic transport. Due to the parallel electronic conductivity, the magnitude of the grain boundary resistance cannot be established from the measurements. The dc point resistance in the impedance diagrams (see Figs. 8 and 9) is given by:

$$R_{dc} = \frac{1}{\frac{1}{R_e} + \frac{1}{R_i + R_{gb}}} \quad (1)$$

When the grain boundary resistance, R_{gb} , is very large with respect to the electronic resistance, R_e , the dc point represents the electronic resistance. In case the grain boundary resistance cannot be ignored, the actual electronic resistance will be larger than the dc point resistance. In this respect, the change in the dc point resistance will reflect changes in both the electronic resistance and the grain boundary resistance.

Because of the small grain sizes of the SF1000 samples, a percolative path through the hematite phase could exist. The relaxation behaviour, observed at 400 °C, must then be explained in terms of a non-equilibrium situation in the hematite phase, i.e. an oxygen deficiency which has been established during the sinterforging procedure and which has been frozen-in during the rapid cooling step. When the samples are again heated, the non-equilibrium situation drives oxygen into the sample by diffusion. This process becomes noticeable at above 350 °C. The difference in relaxation times for the ‘small’ and ‘large’ samples can then be explained qualitatively by the difference in sample geometry.

On the other hand, it may also be the case that the grain boundary layer, whether present as a very thin second phase or as a segregation area at the grain boundaries, is the origin of the parallel electronic conductivity. A possible explanation for the observed relaxation behaviour at about 400 °C could be that the grain boundaries are supersaturated with Fe ions, which will have a higher solubility at the sinterforging temperature (1000 °C). The formation of a new iron oxide phase between the grains will increase the grain

boundary resistance, while the electronic conductivity through the grain boundary area will decrease due to the decrease in iron content. Thus, it is assumed that the newly created phase will not lead to a significant contribution in the electronic conductivity. Another explanation of the decrease in electronic conductivity during annealing could be the retraction of the Fe_2O_3 grain boundary phase. Recent studies on Co-doped cerium gadolinium oxide [24] showed that, for short sintering times, an electronically conductive grain boundary layer could be formed. On annealing at moderate temperatures, a decrease in the electronic conductivity was observed. High-resolution TEM analysis showed a retraction or dewetting of a CoO grain boundary layer during annealing which explained the decrease in the grain boundary conductivity [25]. Although both suggested processes cannot be ruled out completely, a strong argument against is that, in these cases, the relaxation process would be independent of the sample size, unless it involves a reaction with ambient oxygen. This is, however, quite unlikely.

5. Conclusions

The use of identical samples with different geometry has been found to be quite effective for separating surface effects from bulk properties. Decreasing the grain size in 3Y-TZP increases, as expected, the grain boundary resistance. The introduction of a hematite second phase in the sintered compact results in an electronic conductivity. This may be due to enhanced grain boundary conductivity.

Sinterforging two-phase compacts leads, in the case of 3Y-TZP–hematite, thermodynamically to a non-equilibrium situation. Due to the small diffusion distances (i.e. small grain sizes), this leads to relaxation behaviour at moderate temperatures, where the ionic conductivity of the (monoclinic+tetragonal) zirconia phase is sufficiently high to restore the equilibrium oxygen concentration in the hematite-related phases (grain boundary regions and dispersed hematite phase). Also, a much more pronounced electronic conductivity is observed for the sinterforged samples than for the pressureless sintered ones.

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