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Ceramics International 38 (2012) 4813–4818

CERAMICS INTERNATIONAL

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High temperature phase stability and chemical analysis of the highly doped yttria stabilized zirconia with alumina

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Received 6 December 2011; received in revised form 20 February 2012; accepted 21 February 2012
Available online 20 March 2012

Abstract

Short and long term thermal stability of YSZ was studied considering the equilibrium and non-equilibrium phase transformation of YSZ. To improve the long term thermal stability of YSZ, electrical treatment was introduced. Electrical treatment consists of applying electric field into YSZ at high temperatures under a reducing atmosphere. By optimizing the conditions of treatment, electrical resistivity reduced around 40% and thermal stability improved dramatically. These improvements are due to the generation of tetragonal metastable phases. Arguments are put forth to show that electrical treatment induces a relaxation in the lattice. This relaxation is associated with a reduction in lattice tetragonality and replaces the tetragonal grains of YSZ with domain of metastable phases. High resistance of metastable phase to creep deformation and lower electrical resistivity of domains of metastable phases in comparison with tetragonal grains brings about these improvements.

Keywords: Phase stability; YSZ; Chemical analysis; Darkening process

1. Introduction

Solid oxide fuel cell technology is moving forward thanks to the new materials and processing methods employed in their fabrication. Their function is highly dependent upon the electrolyte material and its structure used in these devices. Among several materials tried so far, yttria stabilized zirconia (YSZ) is known as the best material successfully employed in SOFCs which offers a high ionic conductivity thanks to the oxygen vacancies generated with adding the dopant material. This efficiency is, however, limited when material undergoes long period of time at elevated temperatures. Consequently, large destructive volume change occurs due to spontaneous tetragonal to monoclinic phase transition [1,2]. A possible solution to overcome this phase transformation is to stabilize tetragonal metastable phases (t') in YSZ [3]. Crystallographically, the t' phase is identical with the tetragonal phase; however, oxygen is displaced along c-axis of the lattice [4]. Extremely fine domains of t' phase make it highly resistant to martensitic transformation. Therefore, it is not the grain size that matters insofar as martensitic transformation is concerned, but the critical parameter is the domain size [3]. Hence, producing YSZ electrolyte with fine domain tetragonal metastable phase is the goal of this study. There are three methods which might be promising to generate YSZ structured by t' phase such as doping [5,6], quenching from high temperature, and stabilizing the t' phase [7,8]. Quenching and stabilization method will be probed in this study.

Basically, high temperature is required providing the ionic conductivity of the YSZ. In this study, it is pointed out that during the cooling process from elevated temperatures, generated strain from the harder alumina grains compresses the YSZ lattice leading to tetragonal metastable phase transition. Rapid cooling process magnifies the residual stress around yttria segregated particles and increases the density of tetragonal metastable phases within the YSZ matrix. Therefore, by modulating the cooling process, the tetragonal metastable phases in YSZ could be stabilized. However, there is a certain degree of freedom in which higher residual stress than a certain value distorts the lattice such that monoclinic phase appears. This is a limitation of

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0272-8842/$36.00
doi:10.1016/j.ceramint.2012.02.069

quenching technique because the threshold value of stress could not be identified due to its dependence upon fabrication process of YSZ. On a tangent, generating t' phase using applying electric field could be more promising due to controllable nature of the method. Electrical treatment has similarity with blackening process. Blackening of stabilized zirconia caused by strong chemical or electrochemical reduction is a well known phenomenon. Numerous investigations were performed on blackened zirconia (mostly at room temperature), particularly to clarify the nature of the blackened (conductivity measurement [9–12], electron microscopy [13], X-ray studies [14]). Despite these studies the chemical nature of blackened zirconia is still in discussion and attracts further interest [15].

Basically, metastable phases of YSZ are extremely important in the industrial applications due to their excellent resistance to destructive martensitic transformation which is common in large-grained tetragonal phase materials. Besides, its excellent toughness, good strength, and excellent creep resistance make this phase remarkable as well [1]. Because of its properties, the YSZ constructed by tetragonal metastable phases could be superior in terms of high temperature stability which is ideal for elevated temperature applications such as fuel cells and thermal barrier coatings.

2. Experimental

Specimens were made based on tape casting and multilayer planar ceramic technologies through sintering of 4.5 mol% Y_2O_3, 9.4 mol% Al_2O_3, and zirconia (balance) powders, as electrolyte. The starting material is fully tetragonal. To study the effect of thermal treatment and quenching effects, samples were classified into three main groups based on annealing temperature (i.e. 400, 800 and 1000 C). Samples were annealed for 1, 6, 24, and 48 h followed by cooling in air, water, or ice (Table 1). Annealing products were then microstructurally characterized using scanning electron microscopy (Hitachi H-4100FE). The impact of annealing procedure on phase transformations in YSZ samples was investigated through XRD (MRD-Philips, Kα radiation).

To study the effect of applying an electric field at elevated temperature, two Pt-YSZ electrodes were printed on both sides of YSZ. Samples were electrically treated at 1 V, 2 V, and 3 V, at 400 °C, 600 °C, and 800 °C under fully N_2 environment for duration of 10 min applied on 1 cm × 0.5 cm × 1 mm electrolyte effective area. Electrically treated samples were characterized using impedance spectroscopy, X-ray diffraction, High Resolution Transmission Electron Microscopy (HRTEM), and time-of-flight secondary ion mass spectroscopy (TOF-SIMS). Eventually, to understand the effect of metastable phases on high temperature stability, an electrically treated sample was heat treated at 1000 °C for 50 kh and its stability was studied in terms of crystal structure.

3. Results and discussion

SEM images corresponding to two extreme cases (sample 1 with 1 h annealing at 400 °C, air quenched, and sample 36 annealed for 48 h at 1000 °C, ice quenched) are presented in Fig. 1. Apparently, samples are identical in grain size (below 1 μm) and porosity which means that the material is not strongly affected by short time heat treatment microstructurally. This was already anticipated due to the high stability of the material. Basically, the effects of alumina addition upon YSZ are, first scavenging silicon impurities from grain boundaries of YSZ, and second enhancing the mechanical properties of YSZ preventing from cracking during fabrication process. These properties are due to the fact that initially alumina positions within YSZ grain boundaries. Impurities most likely hamper slipping of grain boundaries, strengthening material against destructive shear strain.

Fig. 1(c) depicts X-ray diffractions of annealed YSZ samples (sample 1 with 1 h annealing at 400 °C, air quenched, and samples 12, 24, 36 annealed for 48 h at 400 °C, 800 °C, and 1000 °C all ice quenched). It could be seen that there is no clue for appearance of monoclinic phase and structurally all samples are mostly tetragonal with small cubic phase formation within around 74°. For samples heated up to 800 and 1000 °C, we enter a binary area composed of tetragonal and cubic phases of the material. Upon intense quenching to room temperature and

Table 1
Annealing conditions of as-sintered YSZ.

	Temp (°C)	Time (h)	Quenching environment
1	400	1	Air
2	400	1	Water
3	400	1	Ice
4	400	6	Air
5	400	6	Water
6	400	6	Ice
7	400	24	Air
8	400	24	Water
9	400	24	Ice
10	400	48	Air
11	400	48	Water
12	400	48	Ice
13	800	1	Air
14	800	1	Water
15	800	1	Ice
16	800	6	Air
17	800	6	Water
18	800	6	Ice
19	800	24	Air
20	800	24	Water
21	800	24	Ice
22	800	48	Air
23	800	48	Water
24	800	48	Ice
25	1000	1	Air
26	1000	1	Water
27	1000	1	Ice
28	1000	6	Air
29	1000	6	Water
30	1000	6	Ice
31	1000	24	Air
32	1000	24	Water
33	1000	24	Ice
34	1000	48	Air
35	1000	48	Water
36	1000	48	Ice

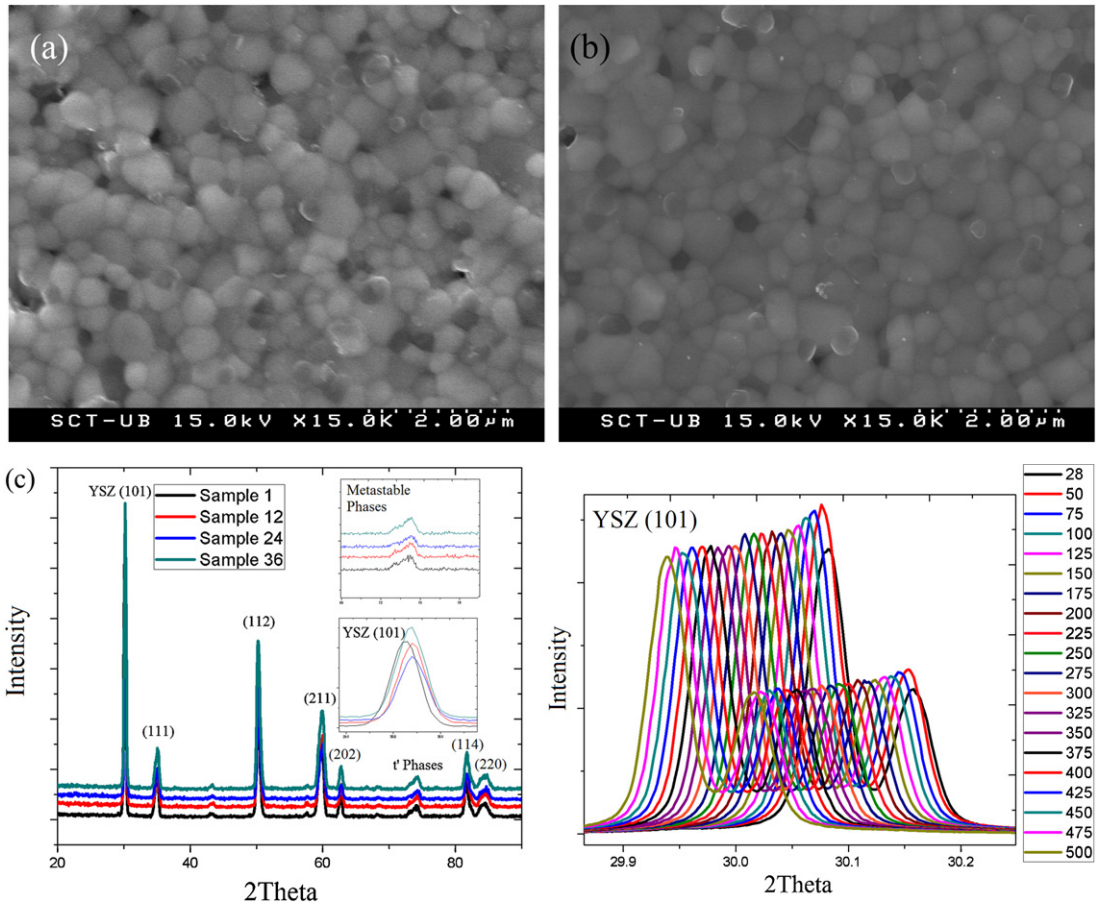

Fig. 1. SEM images of annealed YSZ for 1 h at 400 °C, air quenched (sample 1) (a) and annealed for 48 h at 1000 °C, ice quenched (sample 36) (b). Apparently, samples are identical in grain size (bellow 1 μm) and porosity. (c) X-ray diffractions of annealed YSZ samples metastable phases were detected in all samples whereas shifting of YSZ (1 0 1) reveals the variation of *d*-spacing and generation of metastable phases induced by stress. (d) X-ray diffractions of as-sintered YSZ from 50 °C to 500 °C with 25 °C increments followed by XRD results at room temperature targeting YSZ (1 0 1) diffraction. Linear increase of lattice *d*-spacing of YSZ (1 0 1) reveals that there is no diffusional phase transition induced by temperature.

under equilibrium conditions, a mixture of monoclinic and cubic phases is expected to form. However, XRD patterns reveal the presence of tetragonal crystals ((0 0 4) and (4 0 0) reflections corresponding to t'-YSZ) [8]. This turns out to be a non-equilibrium phase transition in which quenching results into generation of tetragonal metastable phases rather than monoclinic phase. XRD patterns disclose the fact that annealing the samples at 1000 °C results into a shift in (1 0 1) peak toward higher 2θ angles which means that the *d*-spacing between these crystal planes has a decreasing trend. This can be due to the formation of metastable tetragonal phases. Looking more deeply into YSZ (1 0 1), it could be seen that small shifting appeared by increasing the annealing temperature and/or intensifying the quenching environment. To separate the effect of annealing temperature from quenching, thermo-diffractometry was done on as-sintered YSZ, shown in Fig. 1(d). Fig. 1(d) depicts X-ray diffractions at various temperatures raised from 50 °C to 500 °C with 25 °C increments followed by XRD results at room temperature targeting YSZ (1 0 1) diffraction. Reasonable peak shifting corresponds to volumetric expansion due to temperature raise.

Linear increase of lattice *d*-spacing of YSZ (1 0 1) reveals that there is no diffusional phase transition induced by high temperatures. Considering the fact that metastable phase transformation is diffusionless, the effect of stress upon metastable phase formation is more intense. Therefore, treatments in which they modify residual stress within YSZ

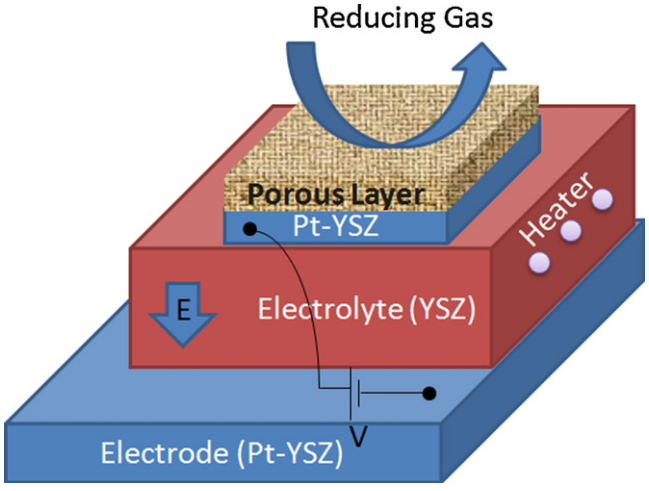

Fig. 2. Schematic illustration of typical YSZ based device and electrical treatment.

Table 2
Resistivity variation upon applying electric field at 800 °C and percentage of resistivity reduction after electrical treatment.

	Initial	After 10 min at 1 V at 800 °C	Percentage
Total R (Ω)	70	68	3%
	Initial	After 10 min at 2 V at 800 °C	Percentage
Total R (Ω)	69	63	9%
	Initial	After 10 min at 3 V at 800 °C	Percentage
Total R (Ω)	69	41	40%

matrix are the best candidates to generate metastable phases of YSZ. One of those is electrical treatment at elevated temperature [7]. Fig. 2 exhibits the schematic of electrical treatment. Implemented heaters control YSZ temperature when potential difference applies between electrodes. Electrical treatment is done under a reducing atmosphere consisting of CO_2, CO, NO, C_3H_8, and N_2. In order to optimize the electrical treatment conditions, treatment was performed under different voltage and temperatures. Table 2 shows the data concluded from impedance spectroscopy measurement of treated samples. Basically resistivity reduces as much treatment was done in higher temperature. It could be seen that after electrical treatment with 3 V at 800 °C, resistivity (most likely electrical) decreased around 40%. This is an interesting result revealing the potential application of this technique in fuel cell application. Fig. 3 shows High Resolution TEM images of electrically treated YSZ with 3 V at 700 °C. Fast Fourier Transform (FFT) of electrically treated YSZ shows larger YSZ

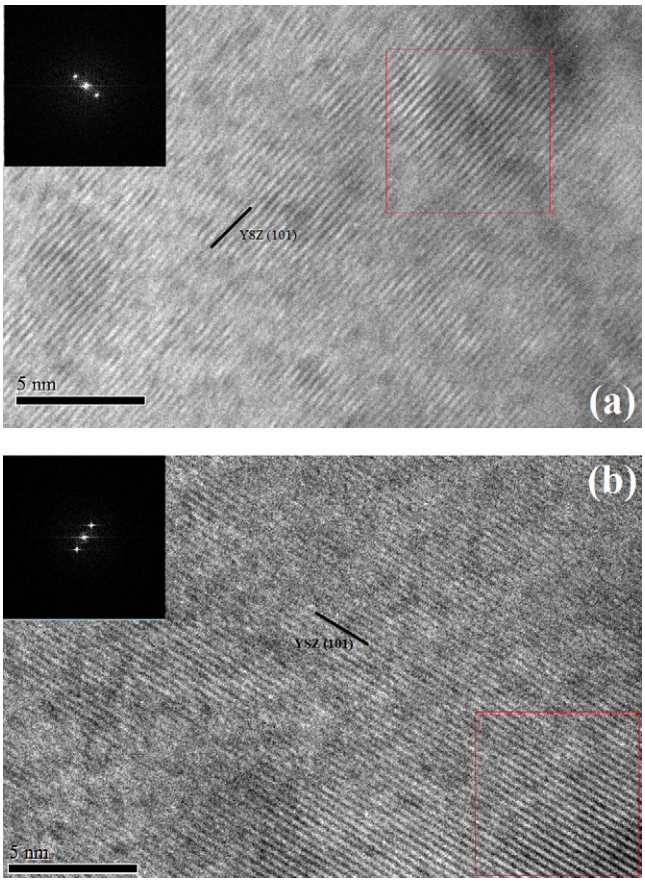

Fig. 3. High resolution TEM of as-sintered (a) and electrically treated YSZ.

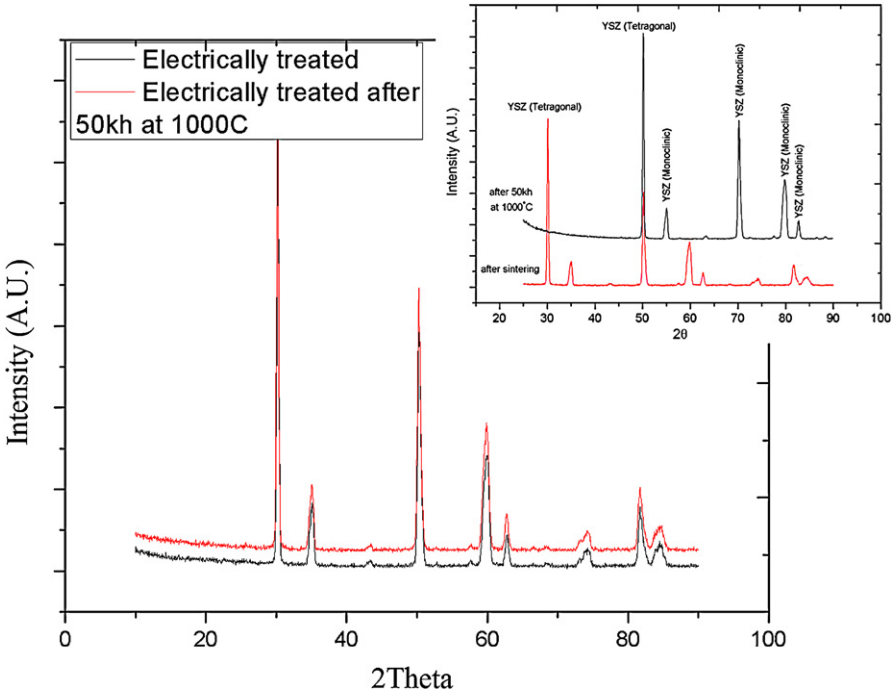

Fig. 4. X-ray diffractions of electrically treated YSZ after 50 kh at 1000 °C. Top right is X-ray diffractions of as-sintered YSZ after 50 kh at 1000 °C. Monoclinic phases could be seen after 50 kh only in as-sintered YSZ and not in electrically treated one.

(1 0 1) *d*-spacing in comparison with untreated YSZ. This is due to the fact that electrical treatment relaxes residual stress within the lattice and stabilizes metastable phases [7]. As a result of electrical treatment and oxygen reduction, tetragonal grain structure of YSZ converts into domains of metastable phase in which lattice *c* parameter of the domain are larger than tetragonal phase and lattice *c* parameter of domain boundaries are smaller than tetragonal phase [8]. Fig. 4 represents the high temperature stability of electrically treated YSZ after 50 kh in 1000 °C. High stability in terms of crystallinity could be seen, however untreated sample (top right image) showed very weak stability, representing large concentration of monoclinic phase. This high temperature stability is due to stabilization of metastable phases because these phases exhibit high resistance against creep. Therefore, it could be concluded that applying optimized electrical treatment increases the thermal stability and life time of YSZ based device such as fuel cell, oxygen sensor, and high temperature electrolyzer. Optimization of electrical treatment results into generation of t' phases in domain boundaries with lattice *c* parameter between tetragonal and cubic. However, applying larger voltage generates darkened areas because reduction causes the crystal to lose O^{2-} ions to be replaced by two electrons and a vacancy, resulting to generation of doubly occupied vacancy. These doubly occupied vacancies generate defect pairs with Y^{3+} [16]. At low level of reduction, light takes one electron from oxygen valence band to one of these defect pairs, producing absorption edge in the material. Upon further reduction, new doubly occupied vacancies appear which do not generate defect pairs with Y^{3+}. This leads to observed coloration [17]. Similar explanation could arise from morphological changes in the interface of Pt and YSZ resulting into enhanced electrical connection between the layers as a result of electrical treatment of the structure [18] and darkening appears [19]. In order to visualize the oxygen migration within the layers, TOF-SIMS was performed. Fig. 5 represents the atomic oxygen intensity variation within layers. It could be seen that the intensity of oxygen reduced after electrical treatment, regardless of polarization direction, which could be due to reducing atmosphere of treatment. Oxygen concentration is almost comparable in electrode layer (Pt-YSZ) of electrically treated sample, however, its concentration in electrolyte (YSZ) increases with moving in depth. Most likely, oxygen concentration will continue to increase up to oxygen concentration in untreated YSZ. This shows that direct electrical treatment removes more oxygen than reverse treatment. Therefore, oxygen vacancy concentration is higher resulting into lower resistivity in comparison with reverse treatment [7]. Fig. 6 represents the variation of oxygen, alumina, zirconia and Platinum content within the top electrode of a fabricated gas sensor which is electrically treated with 3 V and has been worked in real engine for 50 kh at 1000 °C. Fig. 6(a) shows where TOF-SIMS has been performed (Please refer to Fig. 2 for indication of the layers). Fig. 6(b) shows that after electrical treatment, the variation of the oxygen intensity is negligible within electrode layer. This confirms that the electrical treatment could successfully be applied into real

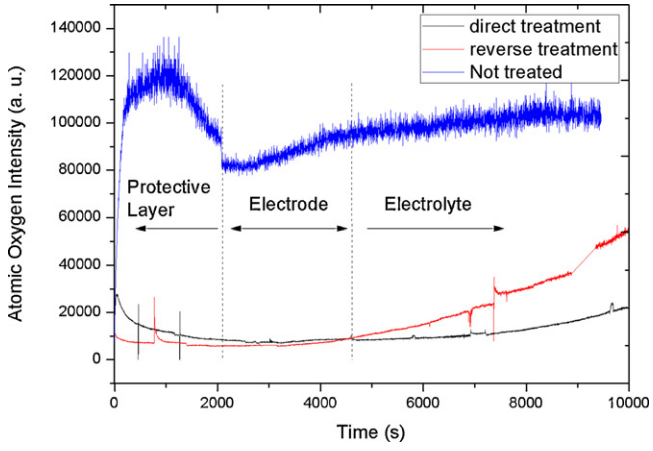

Fig. 5. Variation of atomic oxygen intensity in depth of YSZ based device measured by TOF-SIMS. Signal to noise ratio for untreated sample was quite weak even though the analysis was repeated for several times. In order to facilitate the detection of the different layers, the data corresponding to the untreated sample was drawn with 10× magnitude.

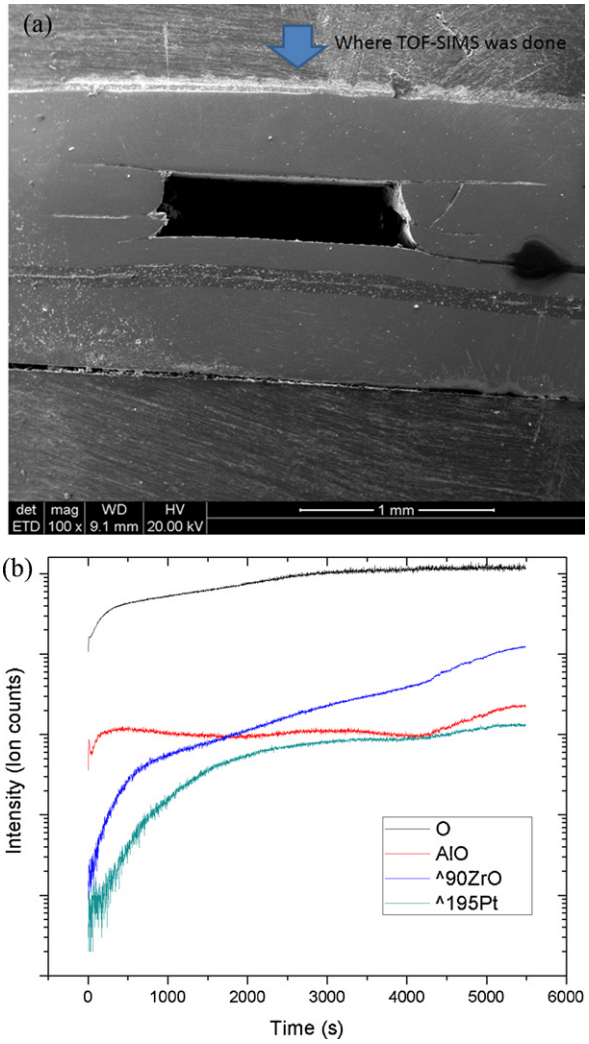

Fig. 6. SEM image of the fabricated and electrically treated gas sensor (a), and TOF-SIMS chemical analysis of the electrically treated YSZ after annealing at 50 kh at 1000 °C. Analysis was performed over the area indicated in (a).

gas sensor. In fact, electric field stabilizes the metastable tetragonal phases which represent a high order of high temperature stability. Moreover, alumina content is quite stable within the top layers showing the fact that 1000 °C does not provide sufficient activation energy for the diffusion of alumina atoms.

4. Conclusion

Initially, thermal stability of YSZ was studied after short time of thermal treatment and its microstructure and phase transformation was analyzed. To probe the long term thermal stability of YSZ, phase transformation induced by applying an electric field through YSZ based device was studied. The absence of a significant change in the YSZ grain size reveals the negligible effect of electrical treatment on the grain growth. Electrical treatment generates domain boundaries consisting of t' phase with lattice c parameter between tetragonal and cubic phase. Applying 3 V into YSZ at 800 °C and under reducing atmosphere showed promising results. Under these conditions, electrical resistivity reduced around 40% which is due to t' phase formation. YSZ constructed by t' phase with appropriate c parameter of lattice exhibits higher thermal stability. Therefore, optimized electrical treatment enhance the life time of YSZ based device as well as great reduction of its electrical resistivity.

Acknowledgment

Albert Cirera is delighted to acknowledge the support from ICREA Academia program.

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