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An enhancement in thermal stability of alumina doped YSZ by applying an electric field

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ABSTRACT

The metastable tetragonal (t') phase in YSZ exhibits significant thermal stability, high strength, excellent toughness and high temperature creep resistance (unlike stable tetragonal phase). Because of its properties, t' phase YSZ would seem to be ideally suited for elevated temperature applications. However, stabilizing of the t' phase is difficult due to its non-equilibrium nature. Electrical treatment is introduced as a method to stabilize metastable phases in zirconia material. Treatment consists of applying an external polarization (3 V) to the YSZ layer at high temperature (700 °C) for 20 min. This process results in a fully t' phase YSZ with the appearance of t'' phase within t' domain boundaries. Arguments are put forth to explain this transformation from the thermodynamic and kinetic point of view.

1. Introduction

Yttria Stabilized Zirconia (YSZ) is the current state-of-the-art material for widespread applications such as thermal barrier coatings, Fuel cell, and oxygen sensors. This material is advantageous because it has a high tolerance for thermal shock, low thermal conductivity, and a higher melting point than most oxides [1]. Yttria stabilizes zirconia in its cubic or tetragonal form and suppresses the tetragonal to monoclinic destructive phase transformation [2]. However, full stabilization to the cubic phase compromises the cyclic thermal fatigue life [3], which is not favourable. Lower dopant concentration stabilizes the tetragonal phase which coexists with tetragonal metastable phases at high temperatures [4]. While cooling, these tetragonal metastable phases transforms into monoclinic phase [5], which leaves behind a volume change [6] resulting in mechanical instability of the material. This process is so called transformation toughening [5]. Therefore, stabilizing the metastable phases at room temperature may suppress transformation toughening. Literary, the term of metastability in tetragonal YSZ is referred to a reduction in tetragonal lattice c value due to the oxygen displacement within the lattice [7].

Previously, Yashima et al. [7] showed that tetragonal YSZ can be classified into three forms, t, t', and t'' and called t' and t'' tetragonal metastable phases. The t' phase grains consist of domains whereas their size is on the order of 100 nm or less. Fine domain size makes t' phase highly resistant to martensitic transformation. Therefore, entirely t' YSZ material exhibits significant thermal stability. Moreover, these materials also exhibit high strength, excellent toughness and high temperature creep resistance (unlike tetragonal phase). Because of its properties, t' phase YSZ would seem to be ideally suited for elevated temperature applications.

This assessment provides a method to stabilize metastable phases at room temperature using an external electric field to be applied to displace oxygen vacancies within the lattice. Previously, quenching from high temperatures was introduced as a stabilizing method [8], which normally leaves behind extensive cracking of YSZ and results in its brittleness. Oversaturation of YSZ with dopants such as alumina might be another method partially stabilizing t' phase [9,10]. However, these two methods face with some limitation in terms of accumulation of residual stress. In fact, previous methods were employed the accumulation of stress to push the lattice and to reduce its lattice c value. In our method, we have tried to stabilize t' phase by applying an electric field at high temperature. Applying an electric field targets directly the oxygen atoms and high temperature facilitates their movement within the lattice. Since, the generation of metastable phases is naturally due to oxygen displacement in the lattice, electrically reduction of YSZ may result in generation of metastable phases. Another advantage of this method is that it is a non-destructive method in contrast with previously applied method. Furthermore, electrical treatment could be applied practically into thermal barrier coating and oxygen sensing industry.

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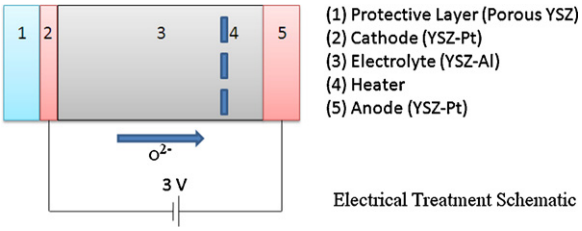

Fig. 1. Schematic of the fabricated specimens and electrical treatment.

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 [11–14], electron microscopy [15], X-ray studies [16]). Despite these studies the chemical nature of blackened zirconia is still in discussion and attracts further interest [17].

2. Experimental methods

4.5 mol% Y_2O_3, 9.4 mol% Al_2O_3, and zirconia were sintered as electrolyte. Pt-YSZ conductive material was used as electrode layers. Final structure was made by means of Tape casting and multi layer planar ceramic technologies [18] (Fig. 1). Specimen was treated electrically. Treatment consists of applying an external polarization to the YSZ layer at high temperature. An external voltage of 3 V is applied between the electrodes; the electrode exposed to the air reference acts as anode whereas the electrode exposed to the reducing atmosphere is the cathode (Fig. 1). The exact bulk gas composition for the electrical treatment was as follow: 10.9% CO_2, 7.3% CO, 460 ppm NO, 4600 ppm C_3H_8, Rest N_2. The heating resistance of the specimen was set at the temperature of the treatment which is 700 °C. The specimen remained under this condition for 20 min.

Raman spectrometry (Jobin Yvon T64000) with a visible Ar+ laser has been used to investigate the zirconia tetragonal crystals.

YSZ layer (electrolyte) was characterized using X-Ray Diffraction (XRD) analyses in θ–2θ scan by means of a 4-circle X-ray diffractometer with Cu Kα radiation (MRD PHILIPS) and High Resolution Transmission Electron Microscopy (HRTEM) (JEOL JEM 2100, 200 kV). Moreover, the nanoprobe EDS measurement were performed with probe size of 0.5 nm at every 1 nm across the grain boundaries in order to identify yttria concentration in boundaries. Impedance spectroscopy (using both Solarton SI-1260 frequency response analyzer and a Gamry Potentiostat PCI4/750) was implemented to compare the electrolyte resistance.

3. Results and discussion

For the sake of simplicity, stabilization could be divided into thermodynamic and kinetic. Thermodynamic stabilization through the free-energy difference (ΔG) is expressed by the equilibrium phase diagram and is responsible for stable phase transformations. However, metastable phases are non-equilibrium. Non-equilibrium phase ($\Delta G > 0$) can be stabilized by the energy barrier, ΔG^* (stabilization by kinetic). Non-equilibrium phases becomes more non-transformable when the energy barrier ΔG^*, is increased, therefore it can remain as a metastable phase or it takes a long time to transform into stable states. The nature of quenching from high temperatures and oversaturation of YSZ with alumina is to increase ΔG^*. Applying an electric field and polarising YSZ will result in an enhancement in ΔG^* as well.

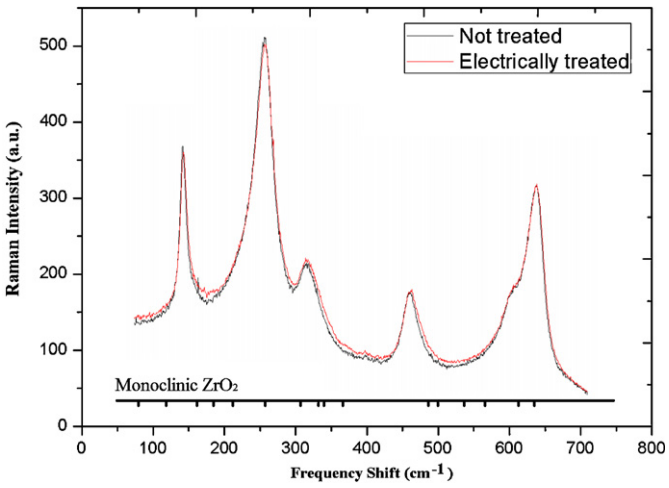

Fig. 2. Raman spectra of as-received and electrically treated YSZ (upper plot).

Fig. 2 shows Raman spectra of as-received and electrically treated YSZ. Undoubtedly, characterization of YSZ with Raman spectroscopy is vital since Raman scattering of tetragonal to monoclinic zirconia is eccentrically strong with unique spectrum. As shown in Fig. 2, Raman spectra of as-received and electrically treated YSZ showed the tetragonal symmetry which has six active modes. No evidence of monoclinic phase is observed. It can be seen that electrical treatment shifts Raman spectra toward higher frequencies though tetragonal structure remains unchanged.

Fig. 3 depicts to the XRD pattern of YSZ before and after electrical treatment. Pattern has been drawn between 2θ position equal

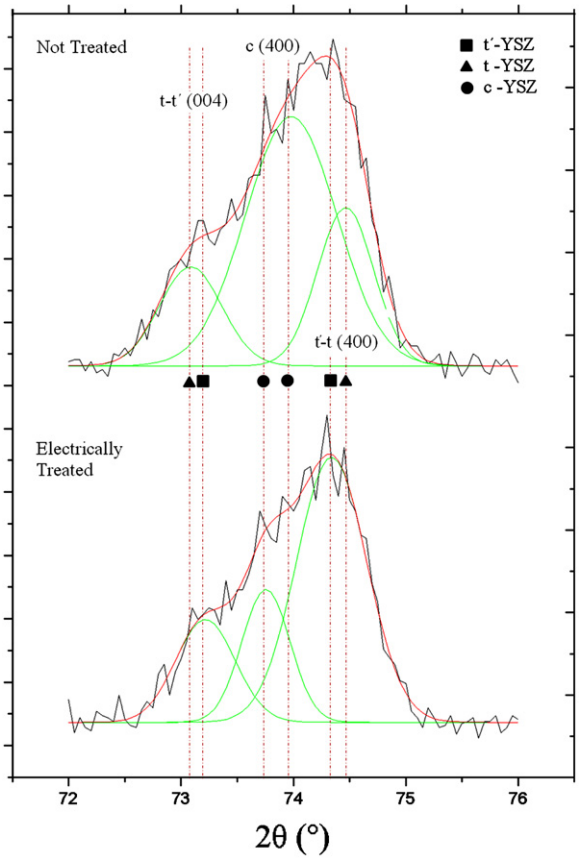

Fig. 3. X-ray diffraction pattern of YSZ before and after electrical treatment. Appearance of t' and t'' after electrical treatment is remarkable.