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Ceramics International 39 (2013) 2535–2543

CERAMICS INTERNATIONAL

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Microstructure and electrical properties of zirconia and composite nanostructured ceramics sintered by different methods

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Received 23 August 2012; received in revised form 3 September 2012; accepted 4 September 2012
Available online 25 September 2012

Abstract

The aim of this study is the preparation and characterization of dense cubic zirconia ceramics and zirconia nanocomposites (reinforced with 5 wt% alumina). The powders were obtained through sol–gel methods and densified using classical sintering and spark plasma sintering (SPS) methods. The obtained ceramics were characterized through X-ray diffraction, scanning electron microscopy and impedance spectroscopy at room and high temperature. The average grain size of cubic zirconia particles was found to be approximately 8 and 2.5 μm for the classical sintering and 99 nm for SPS. The alumina particles in composites have an average grain size of 0.7 μm for classical sintering and 53 nm for SPS ones. The total conductivity for nanocomposites sintered through both methods was also determined.

Keywords: A. Sintering; B. Nanocomposites; C. Electrical properties; YSZ

1. Introduction

Yttria stabilized zirconia with cubic structure is by far the most widely used material for solid electrolytes, and applications could also be found in the ceramic insulators field. The use of these materials is of interest due to their high chemical stability in oxidizing and reducing atmosphere and high conductivity. The solid electrolyte is one of the main components of a combustion cell for high and medium operating temperatures, and the production of high performance materials for the solid electrolytes has been the key factor for an increased efficiency of energy conversion [1].

In stabilized zirconia, part of the Zr^{4+} atoms are replaced by Y^{3+} atoms, with the purpose of stabilizing the high temperature polymorphic modifications of zirconia, thus avoiding the volume variations caused by phase transformations. Moreover, this leads to the creation of oxygen vacancies, which are critical for the electrolyte properties.

The ionic conductivity is directly proportional to the quantity of O^{2-} anions that migrate. The maximum ionic conductivity in the zirconia based systems is observed when the concentration of acceptor type dopant is minimal, with the condition that zirconia is fully stabilized to the fluorine type cubic structure. Although there are many studies concerning electrical performance of yttria stabilized zirconia, most investigations were made on micrometer structured ceramics [2–6]. Consequently, the investigation on nanometric size ceramics and their

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http://dx.doi.org/10.1016/j.ceramint.2012.09.013

composites is necessary, in order to determine what changes in properties occur with the decrease of grain size from micrometers to nanometers.

Composite ceramic materials, with alumina, were prepared, in order to further enhance the mechanical properties of zirconia. In this case, alumina also acts as a sintering aid. Moreover, the electrical conductivity is improved and a lower thermal expansion coefficient is obtained. Also alumina has the effect of lowering the electrical conductivity at grain boundary and an increase in bulk conductivity is observed [7–10].

In the present work, the effect of alumina addition to yttria stabilized zirconia, with respect to electrical properties and microstructure of ceramic samples, for different sintering methods—spark plasma and classical sintering, was studied.

2. Experimental procedure

Cubic stabilized zirconia based ceramics and composites, reinforced with 5 wt% alumina were synthesized and characterized. The amount of yttrium oxide added to the zirconia is of 10 mol%. The zirconia nanopowder was synthesized through a simple sol–gel method, described in previous work. The average particle size of yttria stabilized zirconia nanopowder used is 14 nm [11].

The composite nanopowder was obtained by an unconventional method, schematically presented in Fig. 1, as follows: cubic yttria stabilized zirconia nanopowder, calcinated at 700 °C/2 h, was added to a mixture of alumina nitrate, citric acid and ethylene glycol, in water. The mixture was left on a magnetic stirrer for 120 min at 80 °C, in order to remove water. Gelification also occurred. After that, the gel was heat treated at 700 °C for 120 min, in order to remove all organic residues.

This type of procedure was followed in order to assure a better homogeneity of phases. This is proved through EDX elemental mapping, the results being shown in Fig. 2, for the ceramic powder thermally treated at 700 °C.

By analyzing the elemental mapping on the composite powder it can be observed that the distribution of all elements is highly homogeneous.

The ceramic materials were sintered by classical sintering and "spark plasma sintering" (SPS). In the first case, the powders were shaped by uniaxial pressing, followed by sintering in air, at 1600 °C for 120 min. The SPS obtained samples were first uniaxially pressed into a 30 mm graphite dye, by applying 15 MPa of pressure. After that the graphite dye was placed into the SPS equipment. The sintering temperature used was 1200 °C, with a heating rate of approximately 55 °C/min and the time at the highest temperature was 5 min. The sintering procedure used 110 MPa pressure and inert gas (Ar) atmosphere [12–15].

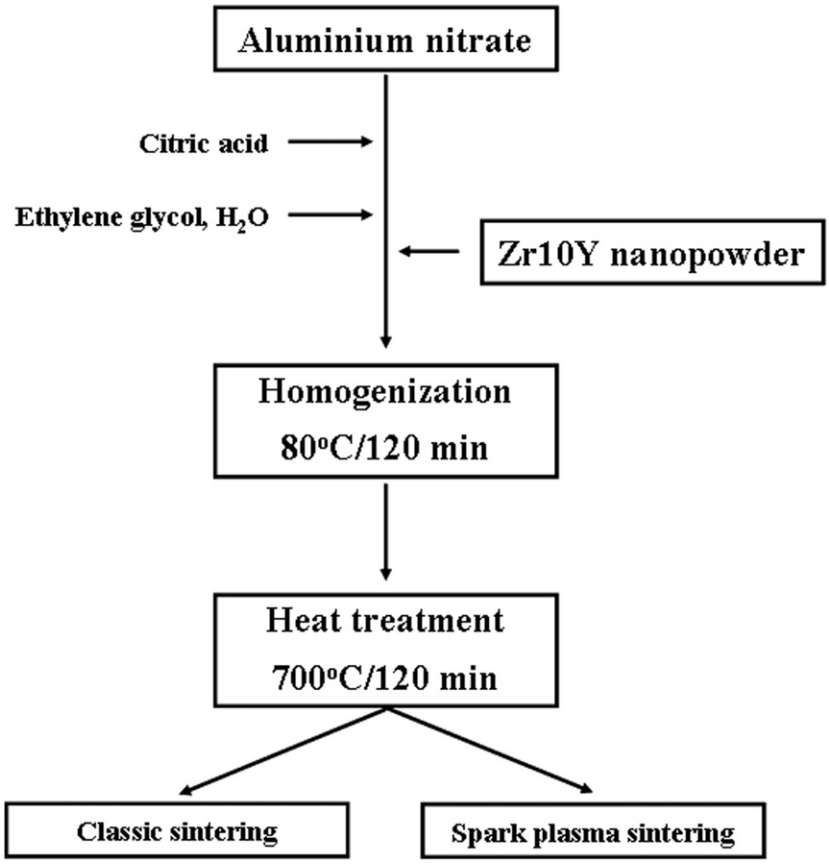

Fig. 1. Technological flow of composite powder preparation.