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Development of zro_2-tio_2 porous ceramic as soil humidity sensor for application in environmental monitoring

R.M.Oliveira; M.C.A.Nono; C.Kuranaga and M.Wada

Grupo de Tecnologias Ambientais - TECAMB
Laboratório Associado de Sensores e Materiais - LAS
Centro de Tecnologias Especiais - CTE
Instituto Nacional de Pesquisas Espaciais - INPE, São José dos Campos - SP – Brazil
Avenida dos Astronautas, 1758, Caixa Postal: 515 - 12.1201 - 970
E-mail: rodmatos@las.inpe.br

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Abstract: Due to the necessity of the automation and control of processes in agriculture, as well as to the crescent interest for the environmental monitoring, efforts have been demanded in the development of more versatile, reliable sensors and sensor systems with smaller cost [1-2]. In this sense, the search of new materials, the modeling study of sensor and the development of new measurement techniques and processing of signs have been orientating the progress in this area [3-4]. In this work, the results of the characterization analyses of sensor elements of ZrO_2-TiO_2 porous ceramic for application as soil humidity sensor, are shown and discussed. These ceramics were obtained from the mechanical mixture of ZrO_2-TiO_2 powders and sintered at 1000, 1100 and 1200 ^oC, for obtaining different porosities. The characterization of the ceramic was carried out using measurements of B.E.T.; nitrogen and mercury porosimetry; scanning electronic microscopy and X-ray diffraction. The porous ceramic characterization as soil humidity sensor element was accomplished through capacitance and impedance measurements using a RLC bridge. The ceramic sensor elements were immersed in the selected and previously characterized soils, the humidities of which were defined in accordance with Atterberg limits, more exactly liquid limit. The results obtained for specific surface area, distribution curves of pore size, microstructure, crystalline phases and sensibility to the soil humidity showed that the ZrO_2-TiO_2 porous ceramic sintered at 1100 ^oC presents a great potential to be applied as sensor element for soil humidity monitoring.

Introduction

The great importance of ZrO_2-TiO_2 porous ceramic as soil humidity sensor is related to its use in the identification of risk - areas, considering the need for acquaintance and follow up of the landslide susceptibility, due to the industrial and urban growth non-properly planned, about which, in Brazil, exist stories dated since 1671 and that have caused, mainly in the last two decades, accidents in some Brazilian cities. The main causes of the mass wasting on hillslopes and correlated processes in the Brazilian environmental conditions are surface and subsurface water regimen; climatic characteristics, with prominence for the pluviometric regimen; characteristics of the use and occupation, including vegetal covering and the different forms of anthropic intervention on the hillsides, as cuts and embankment; pluvial and served water concentration, among others [5]. Other factors can also be cited, as important application for the soil humidity sensors, such as urban and agricultural erosion that promotes situations of risk to the community due to its great destructive power, threatening public habitations and equipment, changing itself into the most detached conditioner for the urban expansion and seating of infrastructure workmanships [6]. The research directed to the study of the water/soil relationships accumulates extensive technical-scientific development, involving different areas of the knowledge, such as, engineering (material, civil, environmental, sanitary, chemical, etc), geology, geography, geomorfology, hidrology, among others, characterizing in appropriate way the multidisciplinariness relevant to the treatment of the environmental subjects [7-8].

The objective of this work is to simulate, in laboratory, mass wasting on hillslopes using Atterberg limits, more exactly liquid limit, that makes the soil a viscous fluid (A. Atterberg and A. Casagrande, 1948) [9], in a condition similar to the reality. The function of the soil humidity ceramic sensor will be to foresee, in advance, the landslide and to prevent a possible catastrophe, using dielectric measurements of capacitance and impedance in function of the soil humidity.

A large variety of soil humidity sensors exists in the market, nowadays, including direct humidity measurement methods, such as gravimetric methods and indirect humidity measurement methods, such as nuclear, tensiometric and electromagnetic methods, for example, neutrons probe, tensiometers, time domain - reflectometry (TDR), frequency domain - reflectometry (FDR), dissipation heat [10]. Both direct and indirect methods however, are very difficult to automatize due to their detection principles, which get difficult the fast environmental monitoring of the risk-areas *in situ* [11-12]. The selection of ZrO_2-TiO_2 porous ceramic was adopted in order to assure the satisfactory operation of the soil humidity sensor, which includes good sensitivity, linearity over the range of application, fast response, low hysteresis and stability to the aggressiveness of impurities present in the environment, leading to a long useful life of the sensor ceramic material [3-6].

This is a matter of great originality in world-wide terms, mainly concerning to the influence of the pores form and pores size distribution on the capacity of chemical and physical interactions of water molecules with the surface of the sensor material.

Experimental Procedure

The ceramic elements of ZrO_2-TiO_2 were obtained from the mechanical mixture of 50% in weight of ZrO_2 and 50% in weight of TiO_2. After they had been mixed, in watery suspension, in centrifugal mill. After the mixture preparation, the material was uniaxially compressed, to a pressure of 100MPa in steel matrix, in the form of tablets (10 approach diameter of mm and thickness with approximately 1mm) in a group of benches of mechanical tests. The tablets had been sintered in the temperatures of 1000, 1100 and 1200ºC for approximately 3 hours in oven type chamber, for obtaining different porosities. A palladium layer was deposited in the two sides of the ceramic tablet, serving as electrode to create the capacitive effect of the sensor. The characterization of the ceramic were carried out using measurements of B.E.T. - Brunauer, Emmett and Teller (specific area of porous), nitrogen and mercury porosimetry (distribution of nano, meso and micropore size), scanning electron microscope - SEM (microstructure) and X-ray diffraction (crystalline phases). The porous ceramic characterization as soil humidity sensor element was accomplished through capacitance and impedance measures using a RLC bridge. The ceramic sensor was immersed in the selected soil, collected in Campos do Jordão/SP, previously characterized as plastic soil, in which were added, in 5 steps of 24 hours each, fractions of the deionized water in quantity of 30.3g, that corresponds to 8.75% of the total soil drying mass, until to reach the soil saturation point (liquidity limit) [12]. At every 24 hours the capacitance and the impedance values were measured. Figure 1, below, presents the experimental procedure flowchart.

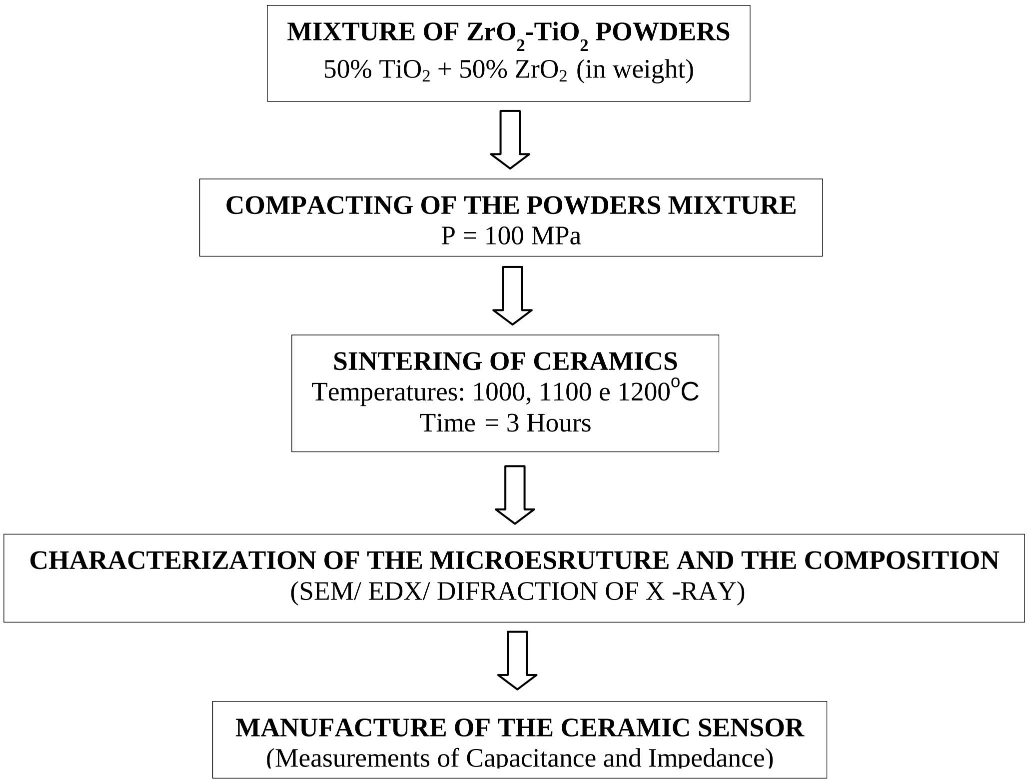

Figure 1. Flowchart of the experimental procedure.

Results and discussion

The analysis of the X – ray difraction presented the presence of the two phases: ZrO_2 e TiO_2. It was proved that, in the sintering temperatures, the two compounds had formed a solid solution (Fig.2).

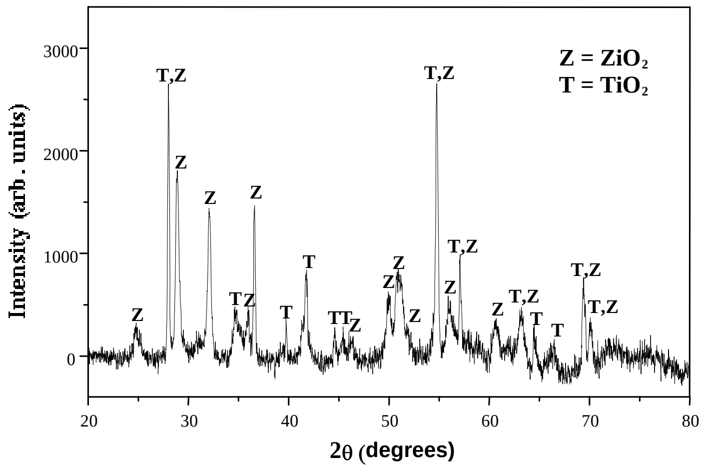

Figure 2. X-ray diffraction pattern of ZrO_2 and TiO_2 solid solution.

A straight relationship between the increase in sintering temperature and the corresponding reduction of the pores specific area was observed, i.e., the ceramic becomes denser and consequently presenting lower porosity (Fig.3a). The curves of pore size distribution with the sintering temperatures are shown in figure 3b.

In the ceramic sintered at 1000°C was found that the pores diameters are under 1µm, with a larger distribution (45cm^3/µm.g) of pore radii in the range from 0.01 to 0.04µm and a smaller distribution (15cm^3/µm.g) of pore radii in the range from 0.3 to 0.9µm 9 (Fig. 3b). In the ceramic sintered at 1100°C was found that the pores diameters are under 1µm, as well, with a smaller distribution (5cm^3/µm.g) of pore radii in the range from 0.01 to 0.025µm and a larger distribution (11cm^3/µm.g) of pore radii in the range from 0.5 to 1µm (Fig. 3b). The ceramic sintered at 1200°C practically presents only one distributions (7cm^3/µm.g) of pores radii in the range 0.9 to 2µm (Fig. 3b). SEM micrographs, with magnification of 3500x, shows the fracture surface of the ceramics sintered at 1000, 1100 and 1200 ºC (Fig. 4).

The results shows, in addition, that the specific surface area and also the pore size distribution analysis were related to the increase in the sintering temperature that promoted the densification of the smaller diameter pore resulting in the presence of larger diameter pores in the ceramic microstructure (Fig. 4).

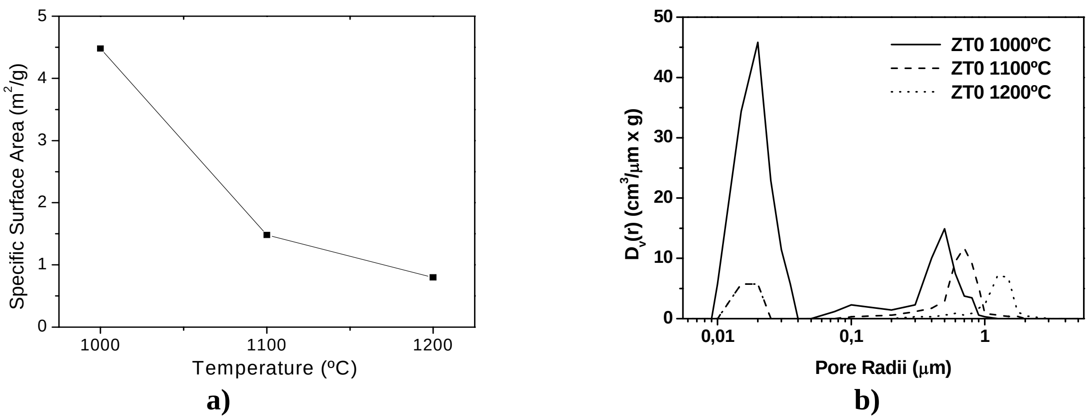

Figure 3. a) Specific surface area of ceramics sintered at 1000, 1100 and 1200 ^{o}C e b) Pore size distribution of ceramics studied in this work.

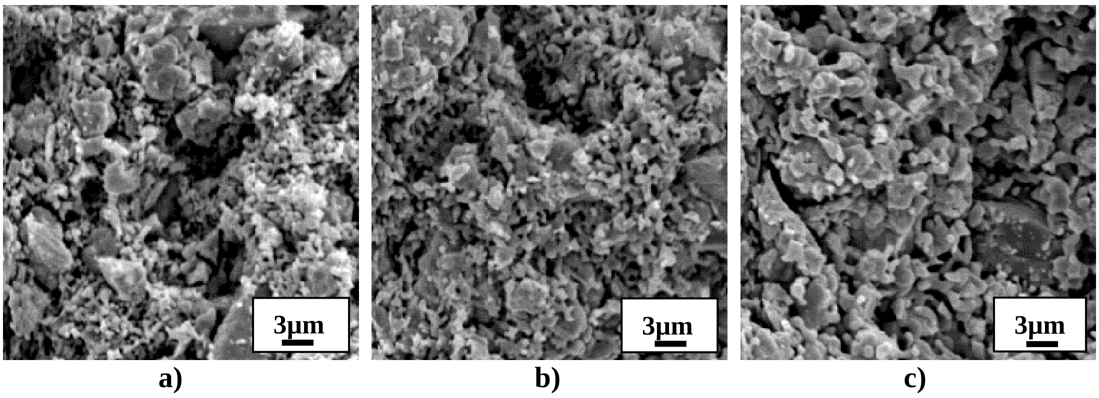

Figure 4. Fracture surface of ceramic sintered at: a) 1000, b) 1100 and c) 1200 ^{o}C.

The capacitance curves of the sensor elements sintered at 1100 and 1200 ^{o}C did not present a tendency to linearity, however, always indicating a typical behavior, showing the increase of the capacitance with the increase in soil humidity and the capacitance curve of the sensor element sintered at 1000 ^{o}C presented a non typical and non coherent behavior, showing the decrease of the capacitance with the increase in soil humidity (Fig.5a). The impedance curves of the sensor element sintered at 1100 ^{o}C presented tendency to linear behavior in the range of soil humidity 1.00 to 26.25% and presented an initial trend to constant impedance in the range of soil humidity 26,25 to 35.00% due to the stabilization due to soil saturation and the impedance curve of the sensor element sintered at 1000 and 1200 ^{o}C did not present a tendency to linearity, however, always indicating a typical behavior, showing the decrease of the impedance with the increase in soil humidity (Fig. 5b).

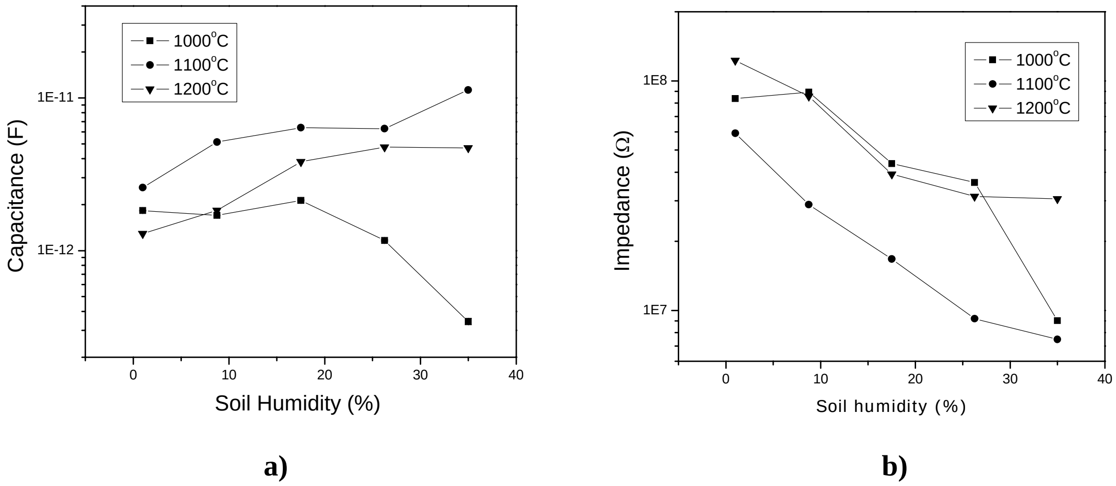

Figure 5. Curves of a) capacitance and b) impedance from sensor elements of ZrO2-TiO_2 porous ceramic sintered at 1000, 1100 and 1200 °C.

Conclusion

From the analysis of the specific surface area and the pore size distribution curves of ceramics sintered at 1000, 1100 and 1200 °C, it can be noticed that the pore volume decreases with the increase in sintering temperature and a reduction in the range of pore diameters distribution occurs. This behavior is coherent with the increase in temperature since there is a trend for a higher coalescence of the particles and the fulfillment of voids to occur, reducing the pore volume.

From the results obtained for the three sintering temperatures, one can see that for the temperature 1100°C, a more homogeneous distribution between large and small pores was obtained, despite, in this case, larger pores were noticed, with radii in the order of 2µm.

The curves obtained from the impedance measurements using a RLC bridge have shown that the sensor element sintered at 1100 °C presented more coherent results with the analyzed literature and were more sensitive to the soil humidity when compared with the curves of the sensor elements sintered at 1000 and 1200 °C and the curves obtained from the capacitance measurements did not present considerable results.

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