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Investigation of the Mechanical Properties of Various Yttria Stabilized Zirconia Based Thin Films Prepared by Aqueous Tape Casting

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ABSTRACT

In this study various yttria doped zirconia based thin films were prepared by the aqueous tape casting method. The rheological property of the paste was studied. The phase content and microstructure of the samples was investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The mechanical properties of thin films were studied by Vickers microhardness and nanoindentation methods. It was found that microhardness, nanohardness and Young's modulus of thin films are not dependent on yttria content, but toughness of the samples was improved by increasing tetragonal phase content of the samples.

1. INTRODUCTION

Yttria doped zirconia (YSZ) are among the most important ceramics, owing to their high mechanical strength, chemical stability and ionic conductivity [1]. Zirconia has three important polymorphs including monoclinic, Tetragonal and cubic. According to ZrO_2–Y_2O_3 phase diagram [2], pure zirconia has monoclinic structure at room temperature with no important application. Addition of 3 mol.% yttria (3YSZ) stabilizes tetragonal phase at room temperature with an excellent combination of high flexural strength (~ 1 GPa) and good fracture toughness (~ 10 MPa $m^{1/2}$) [3]. Zirconia doped with 8 mol.% yttria (8YSZ) has cubic structure at room temperature with highest ionic conductivity among all YSZ ceramics [1]. At concentration of 5 mol.% yttria (5YSZ), both cubic and tetragonal phases can be retained in the microstructure with the best combination of high ionic conductivity and mechanical strength [4]. The YSZ ceramics as thin film, have found applications in technologically important devices, e.g. solid oxide fuel cells and oxygen sensors [1,4]. Improving mechanical properties of zirconia based thin films is crucial to improve the performance and stability of the zirconia based thin films [5]. Various methods have been used to prepare YSZ thin films including Chemical vapor deposition, screen printing, Electrophoretic deposition, etc. [6,7]. Tape casting is a low cost and commercial process for making thin ceramic films for electronic industry, coating, SOFCs, etc. [7]. In tape casting process ceramic slurry is tape cast with a so-called doctor blade on a carrier film with desired thickness [8]. After removing the ceramic tapes from substrate and performing required heat treatments at high temperatures, a ceramic thin film is obtained [8]. It is well known that the processing method affect the mechanical properties of thin ceramic films. There are few studies concerning the mechanical properties of YSZ thin films prepared by aqueous tape casting. The present research aims to study mechanical properties of various zirconia thin films including 3YSZ, 5YSZ and 8YSZ that are provided by aqueous tape casting. In recent years, nanoindentation test method has been used to investigate the mechanical properties of 3YSZ thin films but the results are not consistent [9]. Therefore, in this study the mechanical properties of various YSZ thin films are studied by nanoindentation method. In addition, 3YSZ/8YSZ composite thin films with 25 wt.% 3YSZ has shown interesting electrical properties in bulk and thin film forms [10]. These composite electrolytes have higher electrical conductivity than 8YSZ at low temperatures (T<550°C) which is very important for decreasing the working temperature of solid oxide fuel cells and oxygen sensors [1]. In this research, the mechanical properties of this composite

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electrolyte are also studied and compared with other YSZ thin films. The results would be important to improve the performance and design of zirconia based thin films components.

2. EXPERIMENTAL

Three different commercial powders including 3YSZ, 5YSZ and 8YSZ were purchased from Tosoh Company (Tosoh, Japan). The dispersant was ammonium polyacrylate (Dolapix CE 64, Zschimmer & Schwarz). The 14 wt.% polyvinyl alcohol (PVA, Molecular Weight ~ 55000 g/mol) solution in water and glycerin (99.5%, Merck) were used as binder and plasticizer, respectively. To prepare a stable suspension, 45 g stabilized zirconia powder and 0.3 g dispersant were added to 15 g de-ionized water. The suspension was ball-milled for 24 h using zirconia grinding media at the rate of 60 rpm. To prepare a paste, 4 g plasticizer (9 wt.% based on powder weight) was added to the suspension and the mixture was ball milled at a rate of 6 rpm for 24 h. Then, 3.1 g binder (7 wt.% based on powder weight) was added to the mixture followed by additional ball milling (24 h, 6 rpm). The resulting paste was de-aired under vacuum. Thin films with different thicknesses were cast on a glass substrate by doctor-blade method. The casting speed was 1 cm/s. Four different samples including 3YSZ, 5YSZ, 8YSZ and mixture of 25 wt.% 3YSZ and 75 wt.% 8YSZ (hereafter referred to as 3/8YSZ) were prepared. Rheological data of the paste was recorded using a modular compact rheometer (Physica MCR 300, Anton Paar, USA). Viscosity and shear stress were measured at temperature of 25°C and the shear arte of 10^{-3}-10^{3} s^{-1}, in a loop test. The viscosity measurements were performed on the as-prepared paste. The green tapes were heated to 600°C at rate of 2 K/h and kept at that temperature for 2 h to remove polymeric constituents. The porous tapes were sintered at 1450°C for 2 h. The density of the samples was measured by Archimedean method and thickness of samples was measured by digital micrometer. Phase analysis was carried out on sintered samples by X-ray powder diffraction (XRD, Bruker, D8) using (Cu-$K_{\alpha 1}$= 1.5406 Å) over 2θ range of 26° – 90° with a step width of 0.05°. The microstructure of the polished and chemically etched samples (using hot sulphuric acid) was studied by scanning electron microscopy (SEM, JEOL, JSM-56000). The average grain size was estimated by liner intercept method. Hardness and toughness were measured by Vickers micro indentation method on polished surfaces (down to 1 µm diamond paste) by hardness tester under load of 5 N. The formula of Anstis was used to calculate fracture toughness, using an elastic modulus (E) of 200 GPa. Nanindentation tests were carried out on the polished material surfaces by using a nanomechanical test instrument (Hysitron, Inc.). A three-sided diamond pyramidal Berkovich tip was used as the indenter tip (tip radius 100 nm and tip angle 142.3°). The maximum applied load, holding time and loading/unloading rate .were 5000 µN, 10 s and 135 µN/s, respectively The system has a load and depth sensing resolutions of 1 nN and 0.0002 nm, respectively. The load and displacement were monitored continuously. Young's modulus and hardness were determined from the load–displacement data by using procedure developed by Oliver and Pharr assuming $\boldsymbol{\nu}$=0.3 [9]. All mechanical measurements were performed on thin film with thickness of at least 150 µm to insure that the indenter penetration depth is much smaller than the thickness of the samples.

3. RESULT AND DISCUSSION

In order to obtain dense and defect free thin films by tape casting method, the composition of each component of the paste must be carefully adjusted. According to our results, the optimum composition of plasticizer and binder was 9 wt.% and 7 wt.%, respectively based on powder weight. The fired density of different samples is presented in Table 1. As it shows, all the samples have a relatively high theoretical density which is proper for mechanical properties investigations. The thickness of different samples after sintering was in the range of 50-160µm.

TABLE 1. Density and mechanical properties of various samples.

Sample	Density (%Theoretical density)	Micro-hardness (GPa)	Young's modulus (GPa)	Nano-hardness (GPa)	Toughness (MPa $m^{1/2}$)
3YSZ	98	13.4±.05	210±7	13.9±0.3	5.8±0.2
5YSZ	96	11.6±0.4	190±6	11.7±0.5	3.4±0.3
8YSZ	97	10.8±0.4	188±8	11.3±0.4	1.8±0.2
3/8YSZ	93	11.3±0.5	194±6	11.5±0.5	2.9±0.3

The results of rheological analysis of the paste are presented in Fig. 1. In order to prepare thin ceramics films with suitable properties by the tape casting method, it is very important to control the viscosity and rheological properties of the paste [10]. The amount of water and organic additives in the paste should be as low as possible to minimize the risk of cracking during drying and burn out of the additives [11, 12]. On the other hand, the viscosity of the paste must be low enough in order to ensure a homogeneous mass flow under the blade during the casting process. According to Fig. 1a, the viscosity is decreased due to shear forces and so it can be said that the prepared paste exhibit pseudoplastic behavior which is required for tape casting process [13]. The high viscosity at low shear rates suppresses uncontrolled flow of the paste and prevents sedimentation of the ceramic particles. On the other hand, low viscosities at high shear rates allow easy flow of the paste under the passing blade.

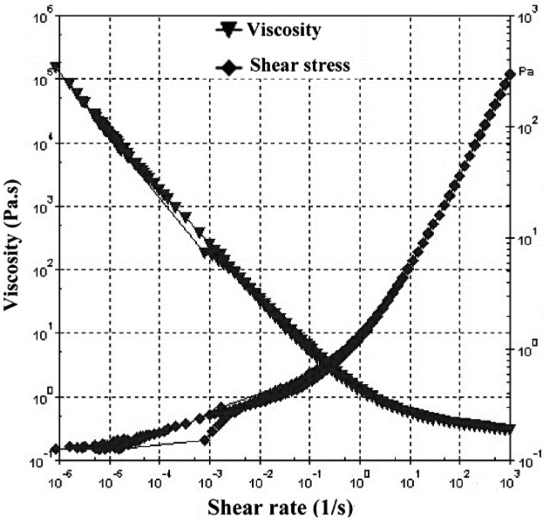

Figure 1. Variation of viscosity and shear stress of the paste as a function of shear rate.

The typical shear rate of the paste under blade in the tape casting process is around 10^2-10^3 1/s. According to Fig. 1, the viscosity values at this shear rate range are around 0.04-0.05 Pa.s which is proper for tape casting process [8].

The results of XRD analysis is presented in Fig. 2. According to JCPDS card numbers 42-1164 and 27-0997, the microstructure of 3YSZ and 8YSZ specimens are composed of only tetragonal and cubic phases, respectively. In addition, the amount of monoclinic phase is not noticeable. On the other hand, the XRD results of 5YSZ and 3/8YSZ samples show that both cubic and tetragonal phases are present in these samples. The XRD patterns of cubic and tetragonal zirconia are mainly superimposed and usually the range of 2θ of 70-80° is used to identify the presence of both phases. Fig. 3 presents the SEM image of different specimens. All samples show a homogeneous microstructure and relatively high density. The microstructure of 3YSZ sample consists of small tetragonal grains with an average size of 0.4 μm while microstructure of 8YSZ is composed of large grain with an average size of about 5μm. It is well documented that the average grain size of tetragonal phase is lower than cubic one and in order to improve mechanical properties, the grain size of tetragonal phase must be less than a critical grain size (~0.5μm) [2]. The microstructure of 5YSZ and 3/8YSZ composite samples show a bimodal grain size distribution composed of fine tetragonal and large cubic grains [1].

The calculated microhardness, nanohardness and toughness of different samples are presented in Table 1. All samples have fairly the same hardness but the toughness of the specimen increases by increasing tetragonal phase content. This is due to the transformation toughening phenomena in which the change of tetragonal to monoclinic phase at a crack tip hinders crack growth and improves toughness [3].

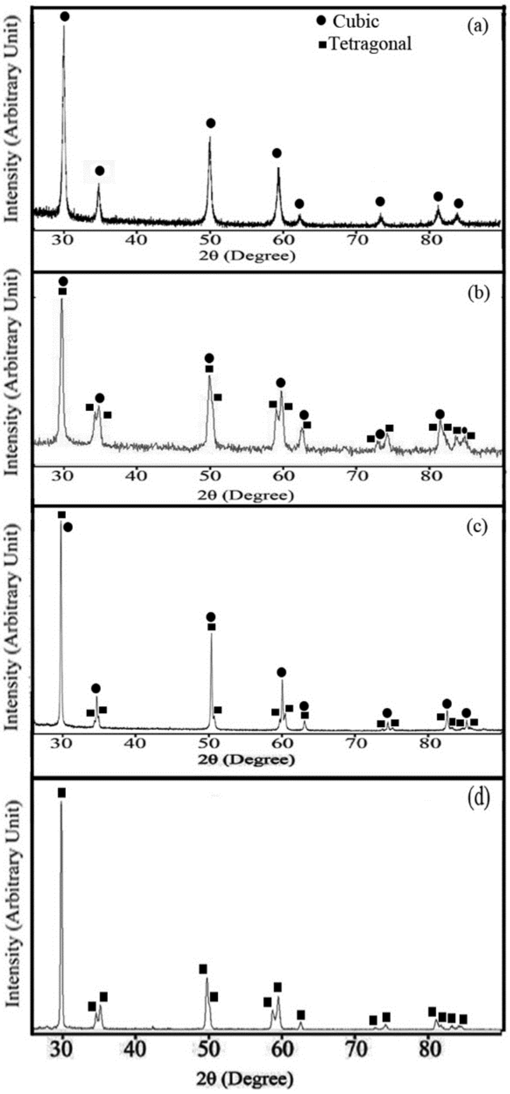

Figure 2. The XRD patterns of (a) 8YSZ, (b) 5YSZ, (c) 3/8YSZ, and (d) 3YSZ.

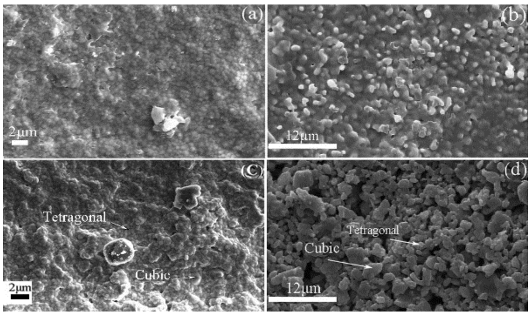

Figure 3. The SEM images of (a) 3YSZ, (b) 8YSZ, (c) 5YSZ, and (d) 3/8YSZ.

In addition, 3/8YSZ sample has mechanical properties comparable with 5YSZ which according to proper electrical properties of this composite [9], makes it attractive for SOFCs applications. The loading and unloading curves of nanoindentaion tests are presented in Fig. 4.

The load and displacement variation curve was recorded. The nanohardness (hardness measured by nanoindentation) was calculated by the following equation [14]:

$$H_c = \frac{\mathrm{P_{max}}}{\mathrm{A(h_c)}} \tag{1}$$

where P_{max} is the peak load and A(hc) is the residual projected area. The value of A(hc) for non-ideal Berkovich indenter is given by Eq. (2):

$$A(h_c) = h_{max} - 0.75\frac{P_{max}}{S} \tag{2}$$

where h_{max} is the maximum penetration depths and S is the contact stiffness which is the slope of the upper portion of the unloading curve. The value of Young's modulus of the samples was calculated according to the analysis of Oliver and Phar [14].

The calculated nanohardness (hardness measured by nanonindentation) and Young's modulus of the samples are presented in Table 1. The values of hardness (micro and nanohardness) and Young's modulus of the samples are fairly the same and are not dependent on yttria concentration. It has been reported that the Young's modulus and nanohardness of YSZ ceramics are not dependent on yttria content but can be affected by the microstructural features of ceramics like porosity [7].

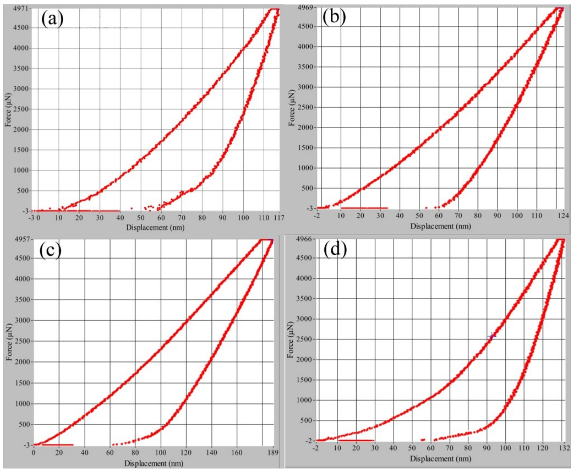

Figure 4. The nanoindentation loading/unloading curves of (a) 3YSZ, (b) 5YSZ, (c) 8YSZ, and (d) 3/8YSZ.

The reported values of Young's modulus for YSZ ceramics measured by nanoindentation method are in the range of 230-260 GPa [15]. It is also reported that the Young's modulus is dependent on penetration depth [16]. The difference between the calculated hardness and Young's modulus may be due to variation in density of materials. According to loading and unloading curves, no pop-in behavior (increase in penetration depth at constant load) is observed and it can be said that all samples have homogeneous microstructure and relatively high density. It is reported that any abrupt change in loading behavior during nanoindentation loading can be due to microscopic inhomogeneities such as pores, phase changes, etc. [14]. The values of Young's modulus are very important in calculation and management of thermal stresses in many important technologically devices like solid oxide fuel cells and oxygen sensors [4].

4. CONCLUSIONS

Thin film of various yttria doped zirconia ceramics including 3YSZ, 5YSZ, 8YSZ and composite of 3YSZ/8YSZ (25 wt.% 3YSZ) was prepared by aqueous tape casting method. The optimum composition for preparation of defect free tapes was determined. All samples had proper density and homogeneous microstructure when sintered at 1450°C. It was found that all the samples have the same microhardness, Young's modulus and nanohardness. In addition, increasing tetragonal phase content of specimen enhanced the measured toughness. The composite of 3YSZ and 8YSZ showed proper mechanical properties and can be considered as a suitable solid electrolyte for fuel cells and oxygen sensor applications.

5. ACKNOWLEDGMENTS

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