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Sol-gel processing of yttria-stabilized zirconia films derived from the zirconium *n*-butoxide-acetic acid-nitric acid-water-isopropanol system

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A stable yttria-stabilized zirconia (YSZ) sol has been synthesized by the controlled hydrolysis of zirconium n-butoxide. Acetic acid and nitric acid were used as chelating agent and catalyst, respectively. The addition of acetic acid and increasing the amount of nitric acids to the system significantly enhanced the sol stability. The viscosity of YSZ sol with the concentration less than 0.80 mol/ℓ was independent on the shear rate, whereas those with the concentration over 1.2 mol/ℓ showed shear-thinning behavior. The reduced viscosity of YSZ sol had linear relationship with sol concentration. These rheological behaviors are attributed to the polymeric nature of YSZ sol. XRD diffractograms of calcined YSZ xerogel confirmed that fully stabilized cubic zirconia phase was formed at a temperature as low as 600°C. Spin coating of YSZ sol on Si substrate followed by heat treatment at 600°C for 2 h in air produced uniform crack-free YSZ films of 70–135 nm thickness.

1. Introduction

Considerable attention has been paid to the application of stable oxide films on nonporous substrates by sol-gel technique to improve the stability of metallic or ceramic surfaces. Sol-gel technology requires less expensive equipment for large-area coatings compared to vapor-phase techniques. In general, it is suitable for protective film formation since relatively dense layers can be prepared at low temperature, and film chemistry can be precisely controlled [1, 2].

Sol-gel processing of zirconia-based thin films has been extensively studied for the protection of metallic substrates against high-temperature oxidation or wet corrosions, due to the high chemical durability and mechanical toughness of zirconia [3–12]. Previously, Atik *et al.* prepared zirconia sol from alkoxide-water-acetic acid system using relatively large amount of water (the molar ratio of water to alkoxide was higher than 10) without acid or base catalyst [4–6]. As a result, the alkoxide was fully hydrolyzed and particulate in nature. Moreover, they applied additional ultrasonic agitation to stabilize the sol. In some efforts of using acetic acid in preparation of zirconia sol, water was not used directly, but esterification reaction between acetic acid and alcohol was used to release water slowly and thus to control the hydrolysis of alkoxide [13]. In that case, nitric acid was added to peptize the sol after esterification reaction was completed. Therefore, the sol was also particulate in nature. Meanwhile, the addition of Y_2O_3 to the zirconia films in sol-gel processing significantly improved the oxidation resistance of stainless steel substrates [6]. Furthermore, yttria-stabilized zirconia (YSZ) films were suggested as thermal barrier coatings on alloy surfaces because YSZ had low thermal conductivity,

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good thermal shock characteristics and thermal expansion compatible with the substrate [14]. Besides metallic substrates, YSZ films have been applied on ceramic electrolyte substrates such as ceria-based oxides to protect the electrolytes against reduction under low oxygen partial pressures [15–17]. Due to their stability and adequate level of ionic conductivity in reducing atmospheres, YSZ films formed by sol-gel method seemed to protect ceria-based oxide substrates from reduction at the fuel-side of a solid oxide fuel cell [17].

The practical application of these sol-gel derived YSZ films, however, will not be realized unless they are made to form uniform crack-free layers on the substrates. It was known that uniform film can be derived from stable sol containing weakly branched linear polymers which, in turn, can be obtained by the controlled hydrolysis and condensation of corresponding metal alkoxides [18–20]. In the case of zirconium alkoxide, however, the hydrolysis is much faster than condensation and, if the process is not properly controlled, the zirconium atoms become fully hydrolyzed, leading to the zirconium hydroxide precipitation that is not desirable for the film formation. One approach to overcome this problem is to control the hydrolysis reaction by using chelating agent that forms strong complex with zirconium atoms, thereby reducing the reactivity of alkoxide and governing the direction of condensation reactions. A variety of β-dicarbonyls, alkanolamines, or carboxylic acids have been suggested as chelating agents in sol-gel processing of zirconia [21–23]. Among them, acetylacetone [10, 13, 24, 25], diethanolamine [14], triethanolamine [26], and acetic acid [4, 5, 7, 27, 28] have been frequently used to prepare zirconia sol. The optimization of the procedure for a metal alkoxide-chelating agent system, however, is a matter of trial and error because the detailed chemical reaction between a metal alkoxide and a chelating agent is not fully understood.

In this research, we studied alkoxide-acetic acid-nitric acid-water-isopropanol system to synthesize highly stable YSZ sol and investigated the effect of acids on the sol stability. A difference from other researches is that the stable polymeric YSZ sol was produced using simpler process. Special attention has been paid to the rheological behavior of sol and the probable nature of sol particles. In addition, we examined the film deposition conditions that produce uniform crack-free layers on non-porous substrate.

2. Experimental

2.1. Synthesis of YSZ sol

Zirconia sol was first synthesized from alkoxide-acetic acid-nitric acid-water-isopropanol system. Zirconium n-butoxide n-butanol complex ($(C_4H_9O)_4Zr \cdot C_4H_9OH$, Alfa Aesar) was used as a starting material which was then diluted with isopropanol (Showa Chemical Inc.) to reduce its viscosity and reactivity with moisture. The molar ratio of Zr: isopropanol in the alkoxide solution was 1:15. The acetic acid (Duksan Pharmaceutical Co.) was added dropwise from a syringe to the stirred alkoxide solution until the molar ratio of acetic acid to Zr became 2, and the solution was stirred for 2 h to let complete the reaction between alkoxide and acetic acid. The catalyst solution containing nitric acid (Junsei Chemical Co.), distilled water, and isopropanol was prepared separately, mixed with the alkoxide solution and stirred for 2 h to produce zirconia sol. The molar ratio of alkoxide:isopropanol in the final solution was maintained at 1:30 while the ratio of alkoxide:water:acetic acid was fixed at 1:2:2. The molar ratio of nitric acid to alkoxide was varied between 0.8 and 1.2. Zirconia sol was also prepared without using acetic acid for comparison. Table I summarizes the reactant composition for synthesizing a variety of zirconia sols in this study.

YSZ sol was formed by adding yttrium salt solution to the zirconia sol. Yttrium nitrate hexahydrate (Aldrich Chemical Co.) was dissolved in isopropanol with a yttrium:isopropanol molar ratio of 1:30 and mixed with the zirconia sol to prepare YSZ sol with the composition corresponding to stabilized zirconia, $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$, after calcination of the sol. After stirring YSZ sol for 2 h in a closed beaker, the sol was passed through a filter (Millipore, Millex-SR, 0.5 μm pore) to remove any solid compounds produced from the reaction between the alkoxide and moisture in the air. The rheological behavior of the sol was characterized by a viscometer (Brookfield, DV-II+).

2.2. Characterization of YSZ xerogel

Thermogravimetric analysis and differential thermal analysis (Setaram, TGDTA92) in air with a heating rate of 1°C/min was carried out on YSZ xerogel to study the weight loss of the sample during the heat treatment. YSZ xerogel was prepared by drying YSZ sol at room temperature overnight. The phase identification and the measurement of nitrogen adsorption isotherm for the YSZ xerogels heat-treated at or above 500°C for 2 h were performed with X-ray diffraction

TABLE I Molar ratio of reactants and stability of the synthesized zirconia sols

Sol number	Molar ratio					Stability[a]
	Zr Alkoxide	Isopropanol	H_2O	HNO_3	CH_3COOH	
Nc1	1	30	2	0.8	0	No
Nc2	1	30	2	1.0	0	Yes
Nc3	1	30	2	1.2	0	Yes
Ac1	1	30	2	0.8	2	No
Ac2	1	30	2	1.0	2	Yes
Ac3	1	30	2	1.2	2	Yes

[a] Clearness in 1 day.

(Rigaku, D/Max3) and BET equipment (Micromeritics, Gemini 2375). The specific surface area and pore size distribution of xerogel were calculated from the nitrogen adsorption isotherms at liquid nitrogen temperature using the BET multilayer model and t-plot method, respectively.

2.3. Film coating and heat treatment

Thin films of YSZ were formed on a silicon (100) wafer of 1 inch diameter by spin-coating method. Spin-coating was performed by placing a few drops of YSZ sol in the middle of the substrate and spinning the sample at controlled rates of acceleration up to 1000 to 5000 rpm for 20 s using a spin-coater (Laurell, WC-200-4NPP). After drying at room temperature for 12 h, the sample was heat-treated at 600°C. The sample was heated at a rate of 0.5°C/min and maintained at the calcination temperature for 2 h, then the sample was cooled to room temperature at a rate 2°C/min for analysis. The morphology and thickness of the films were analyzed by FE-SEM (Hitachi, S-4200) and a He-Ne laser ellipsometer (Gaertner Scientific, L117), respectively.

3. Results and discussion

3.1. Stability and rheological behavior of YSZ sol

Under the experimental conditions employed in this study, zirconia sol was clear right after its synthesis. In order to prevent subsequent precipitation, however, the molar ratio of nitric acid to alkoxide had to be higher than 1 as summarized in Table I. Stability of YSZ sol derived from the clear zirconia sol (Nc2, Nc3, Ac2, or Ac3 in Table I) was investigated by measuring viscosity of the sol with respect to time at room temperature and the results are shown in Fig. 1. Those results revealed that stability of YSZ sol was improved with both the addition of acetic acid (Nc2 vs. Ac2 or Nc3 vs. Ac3) and increasing the amount of nitric acid (Nc2 vs. Nc3 or Ac2 vs. Ac3). The sol synthesized with a nitric acid:acetic acid:alkoxide molar ratio of 1.2:2:1 (Ac3 sol) was the most stable as shown in Fig. 1. The Ac3 sol was clear and stable over six months when stored in a refrigerator kept under 4°C. The stability characteristics of the sol described in Table I and Fig. 1 seem to be attributed to the complexing ability of acetic acid and catalysis effect of nitric acid. It is reported that transition metal alkoxides reacted with acetic acid, leading to the departure of alkoxy group and forming stable metal alkoxo-acetates complexes [21, 22, 27]. Due to its low reactivity, the metal alkoxo-acetate complex hydrolyzed sluggishly, resulting in homogeneous hydrolysis without precipitation. According to the partial charge theory, moreover, the acid-catalyzed condensation of the transition metal complexes is directed preferentially toward the ends of polymers rather than the middles of chains, resulting in less branched polymers [22, 29]. The stability of the sol containing branched polymers is less than that containing linear polymers because the immobilized liquid entrapped within sol particles causes the increase of effective concentration.

TABLE II Physical properties of various YSZ sols formed by solvent evaporation of Ac3 sol

Sol number	YSZ concentration (mol/ℓ)	Density (g/cc)	Viscosity[a] (cP)
Ac3-1	0.45	0.89	3.60
Ac3-2	0.68	0.93	4.75
Ac3-3	0.80	0.95	5.90
Ac3-4	1.19	1.03	9.10
Ac3-5	1.48	1.08	13.70

[a] Measured at room temperature and 60 rpm shear rate.

The viscosity and solid content of YSZ sol were modified by the concentration of stable YSZ sol (Ac3 sol in Fig. 1) through solvent evaporation under vacuum. Five different kinds of sols (Ac3-1–Ac3-5) were prepared as listed in Table II. YSZ concentration in sol increased up to 1.48 mol/ℓ by evaporation while initial concentration of YSZ in the Ac3 sol was 0.45 mol/ℓ. No gelation or precipitation was observed even when the volume of the YSZ sol was reduced to one third of the initial one. The viscosity of YSZ sol was measured with respect to the shear rate and the results are shown in Fig. 2. The sols with YSZ concentration up to 0.80 mol/ℓ had nearly constant viscosity between

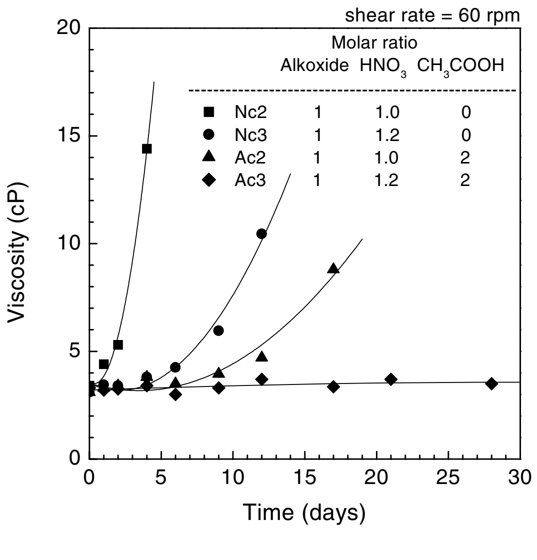

Figure 1 Evolution of sol viscosity with respect to aging time for various YSZ sols.

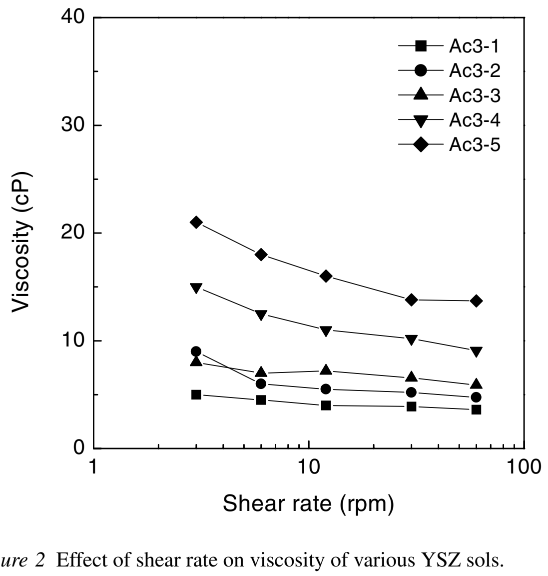

Figure 2 Effect of shear rate on viscosity of various YSZ sols.

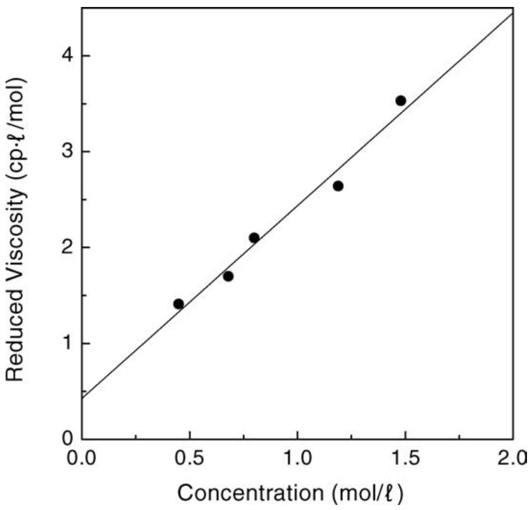

Figure 3 Effect of sol concentration on reduced viscosity of YSZ sol.

5 cp and 10 cp. On the other hand, the sols containing YSZ more than 1.2 mol/ℓ showed shear-thinning behavior. Shear-thinning behavior of the concentrated sol is known to be due to the solvent entrapped within the sol particles that start to aggregate as the concentration increases [30]. At low shear rates, the viscosity of concentrated sol is relatively high because the entrapped solvent is immobile. As the shear rate increases, these aggregated particles break down, releasing immobilized liquid and thus reducing the viscosity.

It is known that the reduced viscosity η_{sp}/C of a dilute polymer solution of non-interacting spherical particles, where η_{sp} is the specific viscosity, is independent of concentration C, whereas linear polymers in dilute solution show a linear concentration-dependence of the reduced viscosity [18]:

$$\eta_{sp}/C = [\eta] + k[\eta]^2 C \tag{1}$$

where $[\eta]$ and k denote the intrinsic viscosity and a proportionality constant, respectively. As shown in Fig. 3, the reduced viscosity of YSZ sol synthesized in this work increases almost linearly with increasing YSZ concentration, suggesting that the sol is composed of linear polymers. The sol composed of linear polymers is preferable for film deposition since interpenetration of the polymers can freely occur in response to solvent removal during gelation, hence promoting dense packing then fine texture. This, in turn, prevents the accumulation of internal stresses associated with the volume shrinkage during the drying process [19, 20].

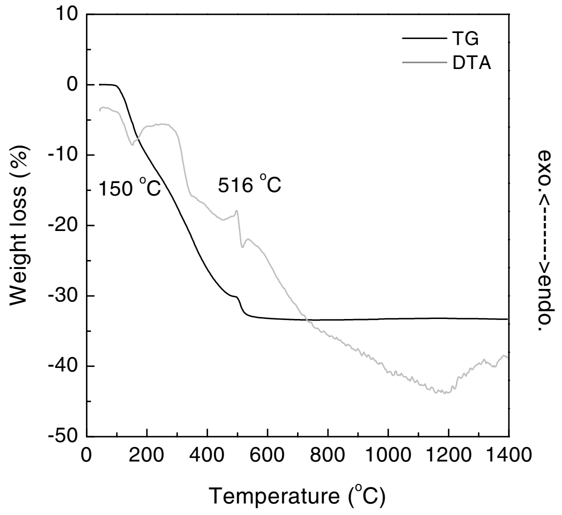

Figure 4 TG/DTA result of YSZ xerogel derived from YSZ (Ac3-3) sol.

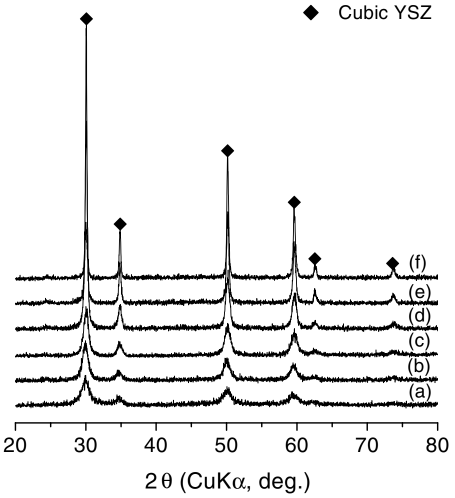

Figure 5 XRD patterns of YSZ xerogel calcined for 1 h in air at: (a) 600°C, (b) 700°C, (c) 800°C, (d) 900°C, (e) 1000°C and (f) 1100°C.

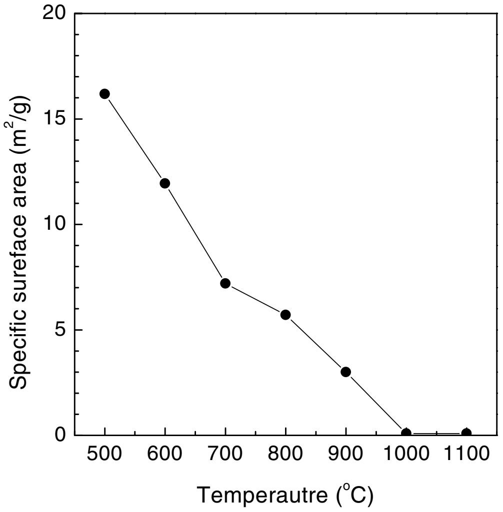

Figure 6 Effect of calcination temperature on BET surface area of YSZ xerogel.

3.2. Properties of YSZ xerogel

YSZ xerogel powders derived from the sol (Ac3-3 in Table II) were subjected to thermal analysis in order to investigate the suitable heat-treatment temperature for YSZ film preparation. Fig. 4 shows TG/DTA results of the xerogel powders, indicating that weight loss of the xerogel terminated near 600°C with two discrete weight loss regions. The weight loss in the temperature range of 100–500°C corresponds to the combustion and decomposition of organic species in the xerogel. The weight loss occurred at 516°C is associated with the decomposition of nitrates that are originated from nitric acid and yttrium nitrates incorporated in sol preparation [31]. There was no change in weight at temperatures above 600°C. XRD patterns of xerogels calcined at various temperatures for 1 h in air are shown in Fig. 5. Fully stabilized cubic zirconia phase was formed at a temperature as low as 600°C. XRD peaks became sharper with increasing the calcination temperature. Fig. 6 shows the

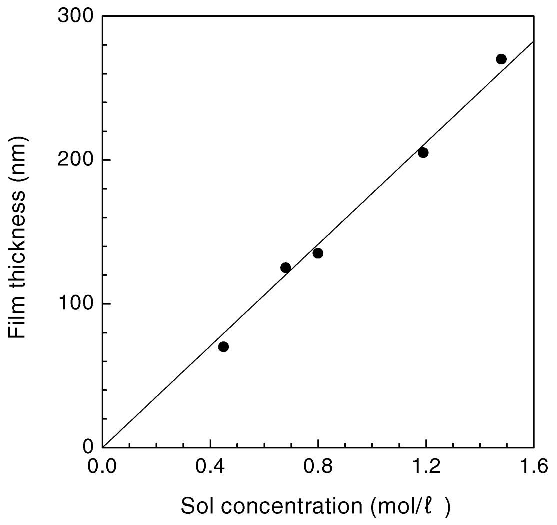

Figure 7 Effect of sol concentration on thickness of YSZ films heat-treated at 600°C for 2 h in air.

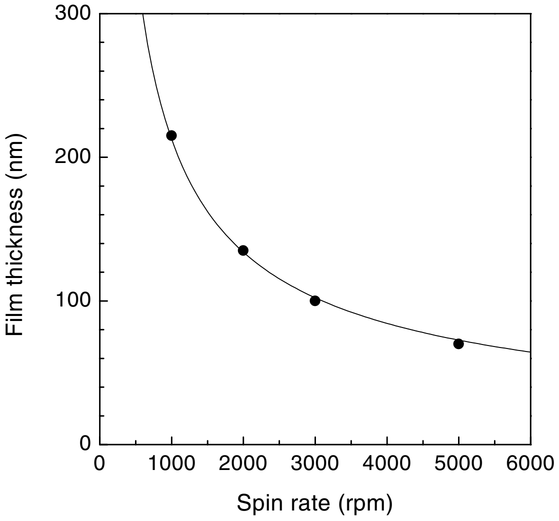

Figure 8 Effect of spin rate on thickness of YSZ film. The film was spin-coated for 20 s using the YSZ sol of 0.80 mol/ℓ and heat-treated at 600°C for 2 h.

evolution of BET surface area of the xerogel with respect to calcination temperature. Specific surface area of the xerogel decreased with increasing the calcination temperature, and became nearly zero when the xerogel was calcined at temperatures above 1000°C. Porosity and the pore size of the xerogel were about 5% and 4 nm, respectively, at temperatures between 600 and 900°C, while those were less than 1% and 2 nm, respectively, after calcination at 1100°C. For dense film application, therefore, it is preferable to perform the heat treatments of the YSZ film at temperatures above 1100°C.

3.3. Effect of spin coating variables on YSZ films

It is known that the thickness and morphology of films produced in a spin coating are affected by a number of the process variables [32, 33]. In the present study, the effects of sol concentration and spin rate on thickness and morphology of the YSZ film were investigated for preparation of uniform, crack-free film on the substrate. Fig. 7 shows the effect of sol concentration on the thickness of YSZ film after the film was subjected to heat treatment at 600°C for 2 h under air atmosphere. In this case, spin coating was performed at a spin rate of 2000 rpm for 20 s. The film thickness increased linearly from 70 to 270 nm with increasing the sol concentration. When YSZ sol with concentration less than 0.80 mol/ℓ was used, the thickness of the film was less than 135 nm and there were no cracks or pinholes in the YSZ films. However, films derived from YSZ sol of 1.19 mol/ℓ with film thickness about 200 nm contained microcracks. The effect of the spin rate on the film thickness was also examined and the results are shown in Fig. 8. In this case, spin coating was carried out for 20 s using the sol of 0.80 mol/ℓ. The film thickness decreased with increasing the spin rate. The films produced at a spin rate of 1000 rpm were thicker than 200 nm, and cracks were observed on the surface. On the other hand, the films prepared at spin rates higher than 2000 rpm had thickness less than 135 nm and did not contain cracks or pinholes. These results imply that spin coated YSZ films with final film thickness less than 135 nm do not produce cracks. Films with thickness higher than 200 nm are prone to cracking probably due to the thermal expansion mismatches between the substrate and film during the drying or heat-treatment process. Fig. 9 shows the surface and cross-sectional SEM micrographs of YSZ film spin-coated for 20 s at 2000 rpm using the YSZ sol of 0.80 mol/ℓ after the heat-treatment at 600°C for 2 h.

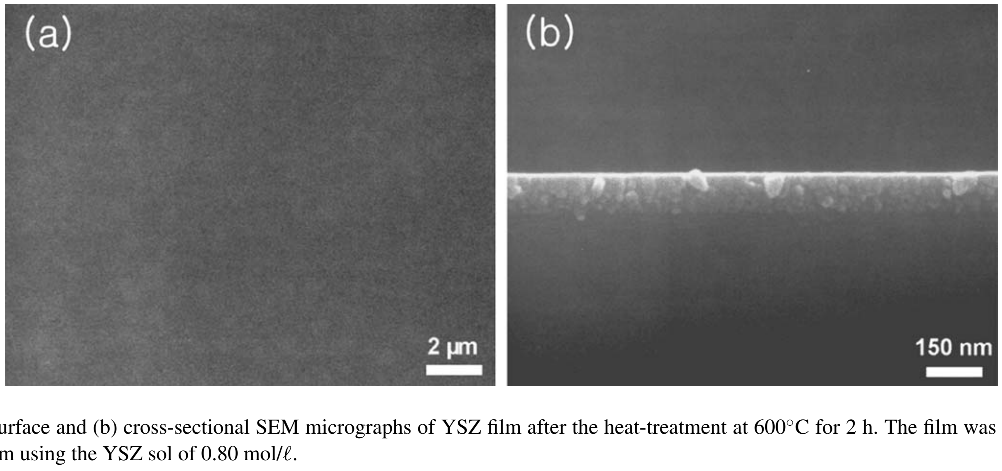

Figure 9 (a) Surface and (b) cross-sectional SEM micrographs of YSZ film after the heat-treatment at 600°C for 2 h. The film was spin-coated for 20 s at 2000 rpm using the YSZ sol of 0.80 mol/ℓ.

4. Conclusion

A stable YSZ sol has been synthesized and applied to a Si substrate to establish deposition process for thin YSZ film coatings on non-porous substrate. The sol was prepared from alkoxide-water-acetic acid-nitric acid system. Acetic acid and nitric acid were used as a chelating agent and catalyst, respectively, to control the hydrolysis and condensation of zirconium alkoxide. It is found that the addition of acetic acid and increasing the amount of nitric acid to the system significantly improved the sol stability. The rheological behavior of the sols with YSZ concentration up to 0.80 mol/ℓ is Newtonian while that over 1.2 mol/ℓ is shear-thinning. The linear reduced viscosity vs. sol concentration relationship indicated that the sol was polymeric rather than particulate in nature. The results of XRD analyses for YSZ xerogel calcined in air revealed that the fully stabilized cubic YSZ phase can be obtained at a temperature as low as 600°C. Spin coating of the YSZ sol on Si substrate followed by heat treatment at 600°C for 2 h in air produced YSZ films of 70–270 nm thickness. It was shown that uniform crack-free YSZ film with thickness less than 135 nm could be formed by applying the sol with concentration less than 0.80 mol/ℓ at a spin rate above 2000 rpm.

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