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Formation of mullite thin film via a sol-gel process with polyvinylpyrrolidone additive

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Abstract

Several tasks were tried to prepare crack-free mullite films on silica substrates. Basically, a sol containing TEOS (Tetraethylorthosilicate) and boehmite colloid was used for spin coating on silica substrate. The formulation of the sols was kept in stoichiometric composition $3Al_2O_3{\cdot}2SiO_2$, or contained a crack-limiting agent, Polyvinylpyrrolidone (PVP). These films were then treated up to 1300°C. The properties of the sols and the dried films were characterized by rheometer, various thermal analysis techniques (DTA, TGA and TMA), also by XRD, SEM and TEM. The mullite film shows randomly oriented grains in sizes from 0.1 μm to a few micrometers. The films still contain fine θ- and δ-Al_2O_3 particles after being treated at 1280°C for 1 h. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Mullite; PVP; Sol-gel processes; Spin coating; Thin films

1. Introduction

Mullite, a high temperature ceramic material, can be synthesized from many methods, such as the reactions of Al_2O_3 with kaolinite, or pure silica with alumina compounds, chemical vapor deposition of Al and Si oxides, etc. According to the report by Schneider et al.,[1] the precursors of these routes can be classified into three types. "Type I" and "type III" precursors are amorphous in the as-prepared state and the former yields mullite as the only crystalline phase at about 980°C, the later only partially transforms to Al–Si spinel at about 980°C. Mullite phase is formed above ~1100°C and extensively at 1250°C. "Type II" precursor contains pseudo-boehmite and non-crystalline SiO_2 in the as-preparation state. Pseudo-boehmite transforms to spinel phase above ~ 400°C and to mullite above ~1250°C. In our previous report,[2] a diphase gel consisted of type II precursors was prepared and characterized. TEOS in acidic and water rich environments forms silica sol with sizes around 20–40 nm.[3] The ultimate mixture of nano-sized silica sol and pseudo-boehmite reduced the formation temperature of mullite as low as 1200°C in appropriate heat treatment condition. The mullitization occurs in accompany with a series transformation of transient alumina.

There are several reports [4–7] mentioning the preparation of mullite thin film. The methods included dip coating of a sol on silica substrate,[4] by spin coating to form an unsupported film,[5] spray pyrolyzing of a precursor on a SiC substrate,[6] or CVD on a SiC substrate.[7] There are some advantages of using sol-gel precursors to form thin film. However, the generation of crack is a problem, because the shrinkage during the drying and thermal stages induces stresses between the coating layer and substrate. To overcome this disadvantage, some additives were chosen,[8–10] like a chelating agent or diols. The major effect of the additives to retard the condensation reaction and promote structural relaxation in the coated films. In the $BaTiO_3$ material system,[10] polyvinylpyrrolidone (PVP) additive was used effectively, increasing the thickness of the coating layer and decreasing the crack formation.

In the present study, a Type II sol was prepared and applied on a silica substrate by the spin coating method. The formulation was adjusted with the addition of the crack-sealing agent of PVP, in order to prevent crack formation. Thermal properties, including thermal shrinkage, thermogravimetric properties during heat treatment, and the microstructures of mullite were investigated.

2. Experimental procedure

2.1. Preparation of the sample

Tetraethylorthosilicate (TEOS, Art. 800658, Merck-Schuchardt, Germany) and pseudo-boehmite colloids (Remal-A20, Remet, USA) were used as starting materials.

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Polyvinylpyrrolidone (PVP) with an average molecular weight of 1300 K g/mol (Acrosorganics, USA) was used as the additive. For the preparation of a basic formulation (abb. TB), TEOS was first mixed with ethanol and hydrolyzed by deionized water under controlled acidic condition (pH = 2.0) by HCl solution. After being fully hydrolyzed, the solution was mixed with pseudo-boehmite colloids and stirred for 1 h.

The thin film sample was spin-coated on silica substrate (GE 124, General Electric, USA) at 5000 rpm for 10 s and then dried at 25°C for 24 h. After dried, the samples were heated to 600°C at a rate of 2°C/min, for dehydration and pyrolysis, and then heated to 1280°C for 1 h. The processing steps of the other formulation containing PVP (abb. TBP) were the same as the TB, except the PVP solution was added in the partially hydrolyzed TEOS solution before it was mixed with pseudo-boehmite. The ratios of each component of the TB and TBP formulas are listed in Table 1. Due to the high viscosity of the PVP solution, the water needed for dilution and successful spin coating for TBP formulation was about 8 times higher than that of TB.

2.2. Characterization

The viscosity of sol was measured by a viscometer (DV-II, Brookfield Co., USA) at 25°C. The thermal analysis was conducted with either differential thermal analysis (DTA), thermal gravimetric analysis (TGA, Du Pont Thermal Analyst 2000 series, USA), or thermal mechanical analysis (TMA, Setsys TMA16/18, Setram Co., USA). The heating rate was 10°C/min for all TGA, DTA and TMA tests.

2.3. Microstructure and phase observation

Two scanning electron microscopes (SEM, Philip XL-30 and Philip 515, Netherlands) and transmission electron microscope (TEM, Jeol CXII-100, Japan) were used to characterize the thickness and microstructure of the films in various heat-treatment stages. The grain size was also measured from the micrographs of TEM with a line-intercept method. The crystalline phases were also studied by X-ray diffractometry (XRD, PW1710, Philip Co., Netherlands).

Table 1
Formulation of two mullite precursors (in molar ratio)[a]

	SiO_2	Al_2O_3	VP	Water	Ethanol
TB	1	1.5	0	28	2.7
TBP	1	1.5	1	228	5

[a] The sources of SiO_2, Al_2O_3 and VP (vinylpyrrolidone) are TEOS, pseudo-boehmite and PVP (polyvinylpyrrolidone) respectively.

3. Results and discussion

3.1. Thermal characters of gels

When the precursors of diphasic mullite were dried and put to heat treatment, there could be a sequence of

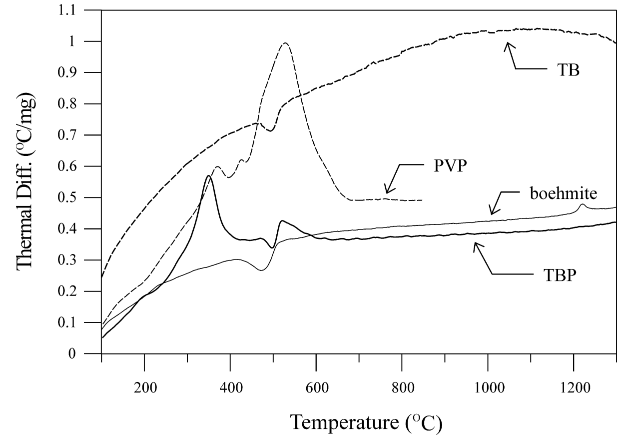

Fig. 1. DTA curves of as-dried TB, TBP, boehmite, and PVP, tested at a rate of 10°C/min.

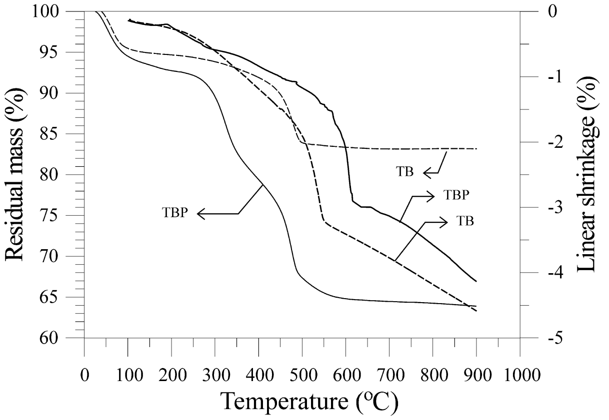

Fig. 2. TMA curves of TB and TBP formulations, tested at a rate of 10°C/min.

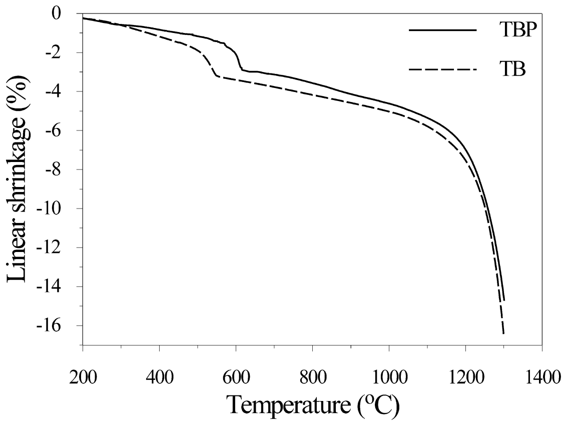

Fig. 3. TMA curves of TB and TBP samples.

reactions taking place, e.g. dehydration and phase transformation.[11] Fig. 1 shows the DTA curves of TB and TBP, as well as two pure materials, pseudo-boehmite and PVP. An endothermic peak appeared in TB curve at 480°C. The peak, compared with the DTA curve of pure pseudo-boehmite, should be a dehydration reaction of pseudo-boehmite phase. However, reaction temperature in the precursory mixture is 20°C higher. The dehydration of pseudo-boehmite phase could be retarded by gel structure.

In the DTA curve of TBP, two exothermic peaks and one endothermic peak appeared. By knowing the thermal evolution of pure pseudo-boehmite and PVP, a large exothermic peak at about 350°C and a second exothermic peak of TBP at 520°C are due to the oxidation of PVP. This polymer is probably pyrolyzed with the catalytic effect by extremely fine SiO_2 gel or Al_2O_3, resulting in low M_w PVP. Therefore, the DTA of partially dissociated PVP has different exothermic temperatures from that of as-received PVP. The endothermic

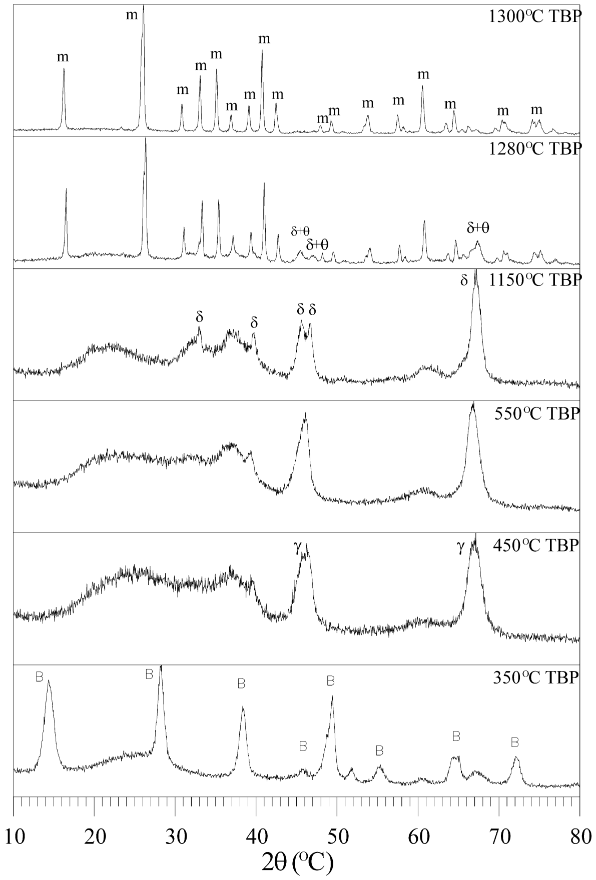

Fig. 4. XRD curves of TBP sample treated at specified temperature for 15 min at 350, 450 and 550°C or 1 h at 1150, 1280 and 1300°C. (B : boehmite; γ: γ-Al_2O_3; m: mullite; δ: δ-Al_2O_3, θ: θ-Al_2O_3).

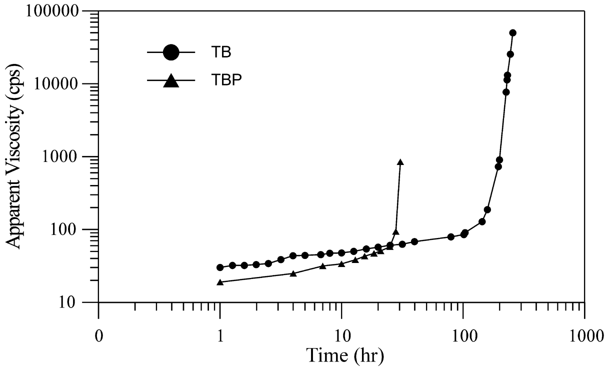

Fig. 5. Viscosity evolution of TB and TBP precursory sols at 25°C.

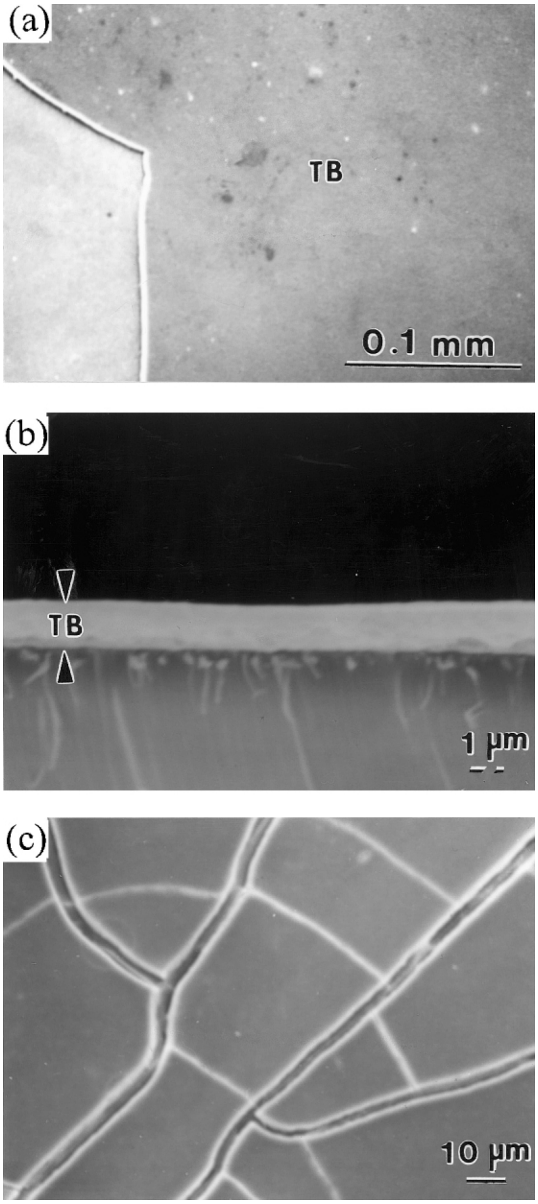

Fig. 6. SEM micrographs of thin film TB sample after 550°C heat treatment: (a) top-view, the right side is a gel layer and the lower left side is silica substrate; (b) cross-section, the thickness of the coating layer is about 1–2 μm; and (c) top-view of the sample sintered at 1280°C.

peak of curve the TBP at 490°C is similar to the one in TB curve, representing the dehydration of boehmite as well.

Fig. 2 shows the TGA and TMA results of TB and TBP samples below 900°C. The TGA curve of TB is shown continuously losing mass until 420°C. The loss rate is then accelerated to 500°C. Above 500°C, the mass remains nearly constant. The TGA results of the TBP sample with PVP are different from the TB sample. The TBP gel shows three steps of mass loss. The first occurs below 100°C. It is the drying of volatile H_2O and ethanol solution. The second mass loss is at about 250–350°C representing the burn out of some low M_w PVP, and the dehydration of silica gel. The third step started at about 450°C and ended about 580°C is the burned-out of the rest of PVP and complete dehydration of pseudo-boehmite. The total mass loss of TBP is ca. 36% higher than that of 16.5% for TB.

Part of Fig. 2 and the whole of Fig. 3 show the TMA curves of TB and TBP samples. Both have two major shrinking stages. The first shrinkage of the curve TB is at about 500–540°C and the second starts from 1050°C. Note that the first shrinkage of curve TBP, as shown in Fig. 2, occurs 80°C higher than that of TB curve. The second shrinkage temperature started at 1080°C is also higher than the shrinkage of TB. The distinct difference of the shrinkage may be due to the response for a better performance of the TBP sample at higher temperature.

The samples shrink ca. $\leqslant 1.5\%$ near 500°C for TB or 580°C for TBP. Both first shrinkage of the TB and TBP are starting at the end of mass loss of their TGA curves. That is possible due to the densification of silica gel or γ-Al_2O_3 grains, or the rearrangement of those fine grains. But the results determined by quantitative XRD can only reveal the evidence of the former case, which show grain growth of γ-Al_2O_3 in the temperature region 500–580°C. It is shown that the width of the X-ray diffraction peak ($2\theta = 67°$) of γ-phase at 550°C in Fig. 4 is reduced compared to that at 450°C. The γ-Al_2O_3 particles grow to a larger size, therefore, narrow down the peak width as well as that of TBP. However, the rearrangement behavior of both phases can not be investigated by present techniques.

Systematical XRD analysis was also carried out to identify the phase evolution of the precursory gels. At these characteristic thermal temperatures of the TBP sample, including 350, 450, 550, 1150, 1280 and 1300°C, the samples were analyzed. When heated at 350°C for 15 min, the crystalline phase of the sample is still boehmite. At 450°C, part of the boehmite is transformed to γ-Al_2O_3. At 550°C, the boehmite phase is gone, but transformed to γ-Al_2O_3. At 1150°C, the δ- and θ-Al_2O_3

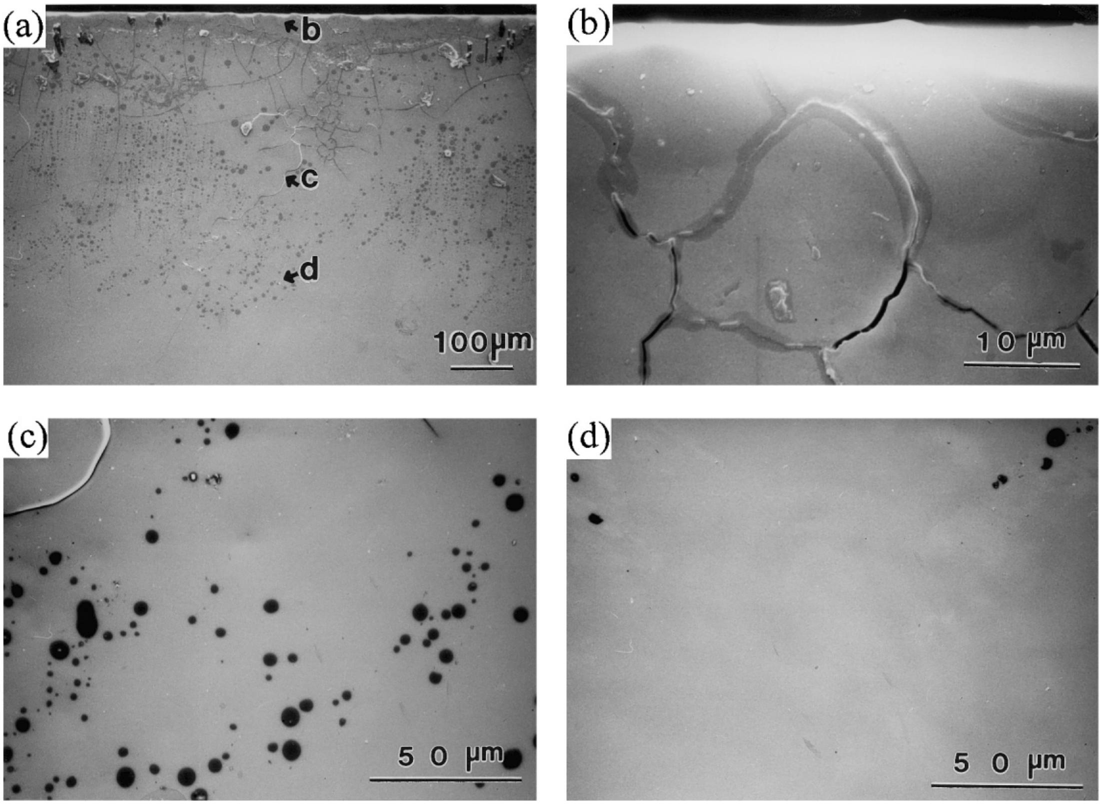

Fig. 7. SEM micrographs of TBP film after 1280°C heat treatment and held for 1 h (a) at low magnification (b), (c) and (d) at higher magnification.

are found in the samples, but the relative quantity of them is not able to differentiated by XRD. At 1280°C, the mullite phase is identified with a minor Al_2O_3 phase. At 1300°C, the mullite is the major crystalline phase and the other crystalline phases are rarely found.

Similar to the phase evolution of TB, the TBP sample with PVP (Fig. 4) contains boehmite and amorphous SiO_2 phase while at temperatures lower than 420°C. But the former changes to γ-phase as the temperature raised. The volatile groups (−OR or OH) on SiO_2 gel [1] and dehydration of boehmite phase [11] are losing mass below 500°C. It is believed that the shrinkage at 580°C is due to the sintering of ultrafine γ-Al_2O_3 as well. In addition to the small shrinkage at 580°C, a second shrinkage starting from 1070 to 1300°C, in a larger scale of 12%, is noted for TBP sample. Two major Al_2O_3 transformations, boehmite to γ-Al_2O_3 and δ- and θ-Al_2O_3/SiO_2 to mullite, are in associated with shrinkage of the diphasic samples.

3.2. Characterization of thin film coating

The viscosity of two diphasic sols is shown in Fig. 5, The basic formulation (TB), which aged at 25°C, would increase its viscosity in 150 h. The gelation point (T_g) of the sol is 150 h at which is the last chance to do a spin coating. Inappropriate usage of sol may induce cracking or ripple surface. The second formulation, TBP, which has a water/ethanol ratio 45.6:1, would have a lower viscosity (~10 cps) at starting point and gradually increase its viscosity until gelling. The gelation point of TBP shows a viscosity ca. 50 cps at 25 h. The coating of the sols is always conducted while the viscosity is less than 100 cps for TB and 50 cps for TBP.

Fig. 6 is a series of SEM micrographs illustrating the surface texture of the TB films originally coated on silica plate. The as-coated film started with a lower-viscosity (32 cps) sol shows no cracks. The cross-section of the film reveals the thickness of ca. 1–2 μm. The film was in the condition without being cracking after calcined at 600°C for 0.5 h. However, the film cracks to mosaic texture while sintered at 1280°C [Fig. 6(c)].

If the formulation of sol changes to TBP, the coated mullite will show better intactness (Fig. 7). The thickness of the layer is also around 1–2 μm. But near the edge of the SiO_2 substrate, there still have some cracks and some bubbles observed next to the region of cracks. The rest of the film is free from cracking.

3.3. Microstructural characterization

Fig. 8 is a set of TEM micrographs of the TBP thin film of formulation sintered at 1280°C for 1 h. The grain boundary of the mullite grain is very wavy which is the typical nature of diphasic mullite. The grain boundaries of the mullite are still irregular, implying that the reaction of residual Al_2O_3 grains (~20–50 nm) with the mullite is not finished yet. The interior of the mullite still contains some of residual Al_2O_3 grains and pores. That is consistent with our previous observation on bulky diphasic gel.[2] But most of the mullite are larger than 0.5 μm and grow in the range of 0.5–5 μm with random orientation, which is proven with the observation of the zone axis of numerous grains. Fig. 9 shows some larger grains on the film near the SiO_2 substrate. The grains are mullite crystals, but appear abnormal acicular in morphology with a long axis oriented parallel to the [001] direction. The abnormal grain growth of mullite is possible due to the melting of silica substrate. The phase offered a favor route for atomic transport during sintering. The grain shape of mullite is plate-like and detailed analysis is needed for further investigation.

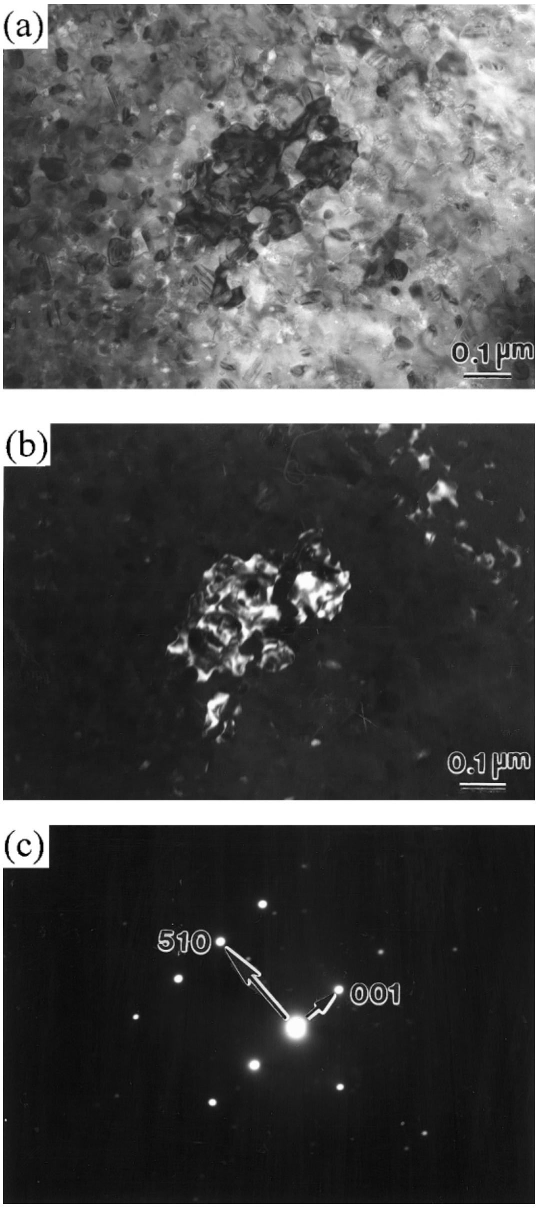

Fig. 8. TEM micrographs of TBP thin film, (a) BF, (b) CDF of (a), (c) DP of the center grain in (a).

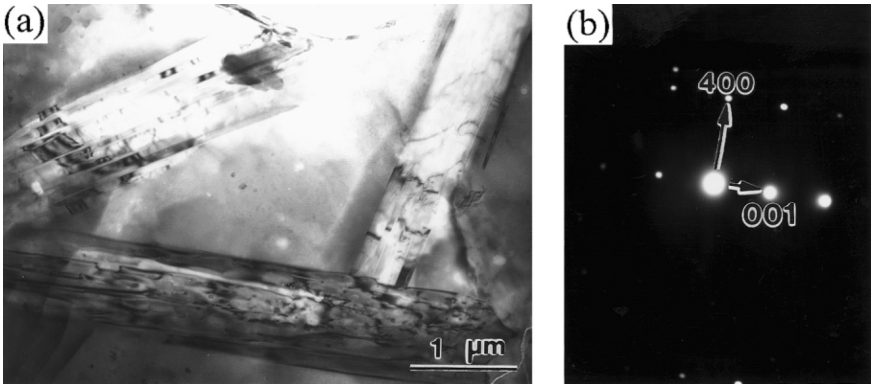

Fig. 9. Abnormal grain growth of mullite on TBP film (a) BF, (b) DP. The grains are grown along the direction [001].

4. Conclusion

PVP is an effective crack-sealing agent for the formation of thin diphasic mullite film. The thermal behavior of TBP is similar to that of TB, besides the burnout of PVP below 600°C and the delay of dehydration reactions. The mullite phase appears at temperatures above 1280°C. Minor residue of Al_2O_3 in mullite grains are found if held at 1300°C for less than 1 h. Uniform film prepared from the TBP sol can be obtained after sintering to 1280°C. The mullite grain morphologies of thin film (TBP) samples are equiaxial, but may grow to platy shape with a plane parallel to the direction [001] of mullite crystal. The grains in thin film are all in sizes around submicrometer to micrometer and randomly oriented, which are similar to the microstructural features of a bulky mullite sample.

Acknowledgements

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