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Sintering behaviour of (Y_2O_3–ZrO_2 gels)

X.M. XI, X.F. YANG
Materials Engineering Program, Auburn University, AL 36849, USA

The sintering behaviour of yttria-stabilized-zirconia (YSZ) gels prepared by a sol–gel process has been studied. The YSZ gels in the forms of bulk and film were sintered at various temperatures up to 1300 °C and the crystalline structures and microstructures were examined by X-ray diffraction and scanning electron microscopy (SEM).

1. Introduction

Fabrication of ceramics through a sol–gel technique has shown many advantages over conventional routes [1]. A typical sol–gel process consists of three stages: (i) solution preparation, (ii) gel formation, and (iii) conversion of the gel to a porous ceramic. Due to the flexibility in the gel formation stage, ceramics in a variety of forms can be prepared by a sol–gel process, including thin films, coatings, fibres, membranes, and bulks. A gel-converted ceramic is porous and can be viewed as an assembly of ultrafine particles with diameters as small as a few nanometres. Such a nano-scale porous ceramic offers many attractive properties. For example, the high driving force and excellent kinetics conditions for densification may greatly reduce the sintering temperature for densification; the nano-scale porous ceramics are also excellent membrane materials for high temperature separation between gases, liquids and solids [2]. It is estimated that the Western world market for advanced membrane systems will total $4.6 billion by 1995 [3].

To exploit these opportunities, it is essential to understand the behaviour of the ultrafine particles and the pores during sintering or service at elevated temperatures. Yoldas [4] has shown that transparent bulk alumina can be prepared using a sol–gel technique, but the sinterability is very poor, reaching only 62% of the full density after sintering at 1200 °C. Kumagi and Messing [5,6] found that the poor sinterability is caused by the significant grain coarsening during the phase transformation from θ-Al_2O_3 to α-Al_2O_3. By seeding with fine α-Al_2O_3 or α-Fe_2O_3, the coarsening associated with the phase transformation is reduced and the sinterability can be greatly improved [7,8].

In the present work we investigate the sintering behaviour of yttria-stabilized-zirconia (YSZ) gels in both bulk and film forms. The YSZ was chosen for its excellent properties and wide applications in many areas. Attention is focused on the microstructure evolution of the gels at elevated temperatures. The results offer useful information for the preparation of porous ceramic membranes and dense ceramic components by a sol–gel process.

2. Experimental procedure

The sol–gel solution was prepared by following Sakurai *et al.*'s method [9] with some slight modifications. A 30 wt % aqueous solution of hydrogen peroxide (H_2O_2) was added to a vigorously stirred 80 wt % butanol solution of zirconium *n*-butoxide, forming a milky solution. Then nitric acid (HNO_3) was added to the vigorously stirred milky solution at a H_2O_2:HNO_3:$Zr(OBu^n)_4$ molar ratio of 10:1:1. A desired amount of yttrium nitrate $Y(NO_3)_3 \cdot 5H_2O$ was added to the stirred mixture to prepare an 8.8 mole %-yttria-doped zirconia sol. After being stirred for about 48 h at room temperature, the mixture turned into a transparent sol. The sol was then evaporated to dryness at 60 °C in a vacuum oven. Finally, a transparent sol with an equivalent zirconia concentration of 0.6 M was obtained by redispersing the dried sol in ethanol.

YSZ films were prepared by spin-coating of the sol–gel solution on fused quartz substrates (25 × 25 mm^2). A film was obtained by dropping the 0.6 M solution through a pipette on the substrate that was spinning at 4000 r.p.m. in a spin-coating apparatus (model EC101DT, Headway Research, Inc.). A spin time of 1 min was used for all coatings. To investigate the effect of the film thickness on the sinetering behaviour, films of different thicknesses were prepared by applying multiple coatings. This was achieved by spin-coating a new layer on the previous one that had been dried in approximately 40 °C air for 3 min. Films with 1, 3 and 20 layers were prepared. The films were heated in a box furnace at a heating rate of 20 °C min^{-1} to 150 °C and held for 10 min, and then further heated to 400 °C and held at temperature for 1 h. Finally, after the heat treatment, the films were examined using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The three films were subsequently heat treated four times at a heating rate of 20 °C min^{-1} to 900, 1100, 1200 and 1300 °C, respectively, and the holding times at all temperatures were 1 h. All three films were examined between two heat treatments using SEM and XRD.

Bulk YSZ samples were also prepared by evaporating the 0.6 M sol–gel solution to 1 M and then casting into teflon bottles. The samples were allowed to dry at

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room temperature for one month. The bulk samples cracked into small pieces, each approximately 3 mm wide. Some fragments were then heat treated in a box furnace at a rate of 1 °C min^{-1} to 400 °C and held at temperature for 1 h. Several fragments were further heat treated four times at a heating rate of 20 °C min^{-1} to 900, 1100, 1200 and 1300 °C, respectively. The holding times at all four temperatures were 1 h. Between two heat treatments, the microstructures and crystalline structures were examined using SEM and XRD.

3. Results and discussion

3.1. Sintering behaviour of the films

X-ray diffraction analysis of the YSZ thin films coated on the fused quartz substrate indicated that the crystallization started between 400 and 450 °C and was completed between 450 and 500 °C. The crystalline structure was cubic and no further phase transformations were detected in subsequent heat treatments to 1100 and 1300 °C (Fig. 1). The thickness of each coating layer is approximately 50 nm after crystallization. The appearances of the films after sintering at different temperatures were compared in Fig. 2. As shown in Fig. 2 (a1, a2, a3), all three films (with 1-, 3-, and 20-layers) sintered at 400 °C are smooth and crack-free (some dusts on the films were intentionally selected for focusing; no grains and pores can be clearly identified. According to our previous experience, the resolution of our SEM observation is better than 30 nm. The films after 400 °C sintering were therefore quite "dense" and were free of pores larger than 30 nm. This observation is in agreement with the usually reported microstructures of other types of ceramics converted from gels.

After sintering at 900 °C for 1 h, the 1-layer film cracked whereas the 3-layer and 20-layer films were still smooth and crack-free (Fig. 2 (b1, b2, b3)). In all films grain texture could be identified. As the sintering temperature increased to 1100 °C, particles with sizes of 50–70 nm could be clearly identified in all three films (Fig. 2 (c1, c2, c3)). The particles distributed themselves uniformly across the whole film and the pores between the particles could also be identified. No particle agglomeration (or aggregation) could be distinguished, and no pores larger than the particles were observed. Apparently, the films after sintering at 1100 °C for 1 h consisted of densely packed particles with diameters of 50–70 nm, except that cracks formed in the 1-layer film. The particle size did not appear to increase much as the sintering temperature rose to 1200 °C (Fig. 2 (d1, d2, d3)). The pores between the particles have become more visible in the SEM observation. The crack openings in the 1-layer film increased as the sintering temperature increased from 900 to 1200 °C. However, no such cracks were found in the 3-layer and 20-layer films after the 1200 °C sintering. To investigate the effect of a prolonged sintering time, one 20-layer film was sintered at 1200 °C for 20 h and still no cracks were observed (Fig. 3).

After sintering at 1300 °C films had shown dramatic changes. The 1-layer film sintered at 1300 °C for 14 h had completely changed its appearance (Fig. 2 (e1)); the particles in the film had shrunk into groups and the gaps between two adjacent groups became approximately 1 μm wide; within each group, grains of the size of 0.2–0.4 μm could be clearly identified, but the grains within each group were not closely packed. Clearly, the seemingly dense film sintered at temperature below 1300 °C was *actually* far from dense, and the film exhibited a considerable shrinkage on the subsequent sintering at 1300 °C. Since the film was bonded to the substrate, it could not shrink freely to increase its density; meanwhile the shrinkage of the film could not be compensated by diffusion in the thickness direction because the film was too thin. As a result, the film formed shrinkage cracks, which widened as the sintering temperature increased. This cracking phenomenon is generally called constrained-sintering cracking and has been reported in other types of films prepared by ceramic powder processing [10–13].

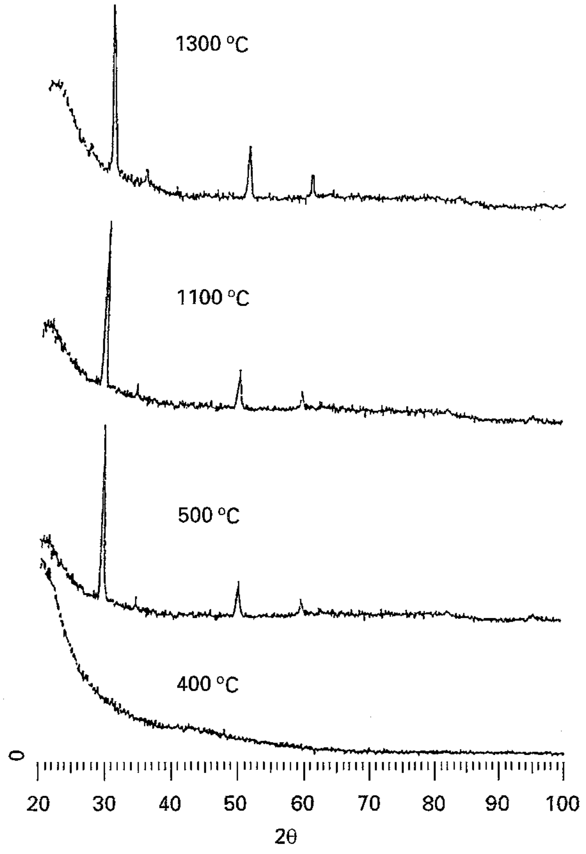


Figure 1 The X-ray diffraction of YSZ thin films after sintering at different temperatures.

Shrinkage was also experienced by the thicker films. The shrinkage could, however, be compensated for by diffusion in the thickness direction and thus the shrinkage became less visible. As a result, no cracks were observed at sintering temperatures below 1300 °C. Evidence supporting the postulation that thick films shrink in the thickness direction was clearly observed in the 20-layer film after sintering at 1300 °C for 1 h (Fig. 2 (e3)); the previously smooth and flat film surface had become full of voids, which apparently were a result of the film shrinking in the thickness direction. In the regions with voids, microcracks appeared. From the micrograph of higher magnification in

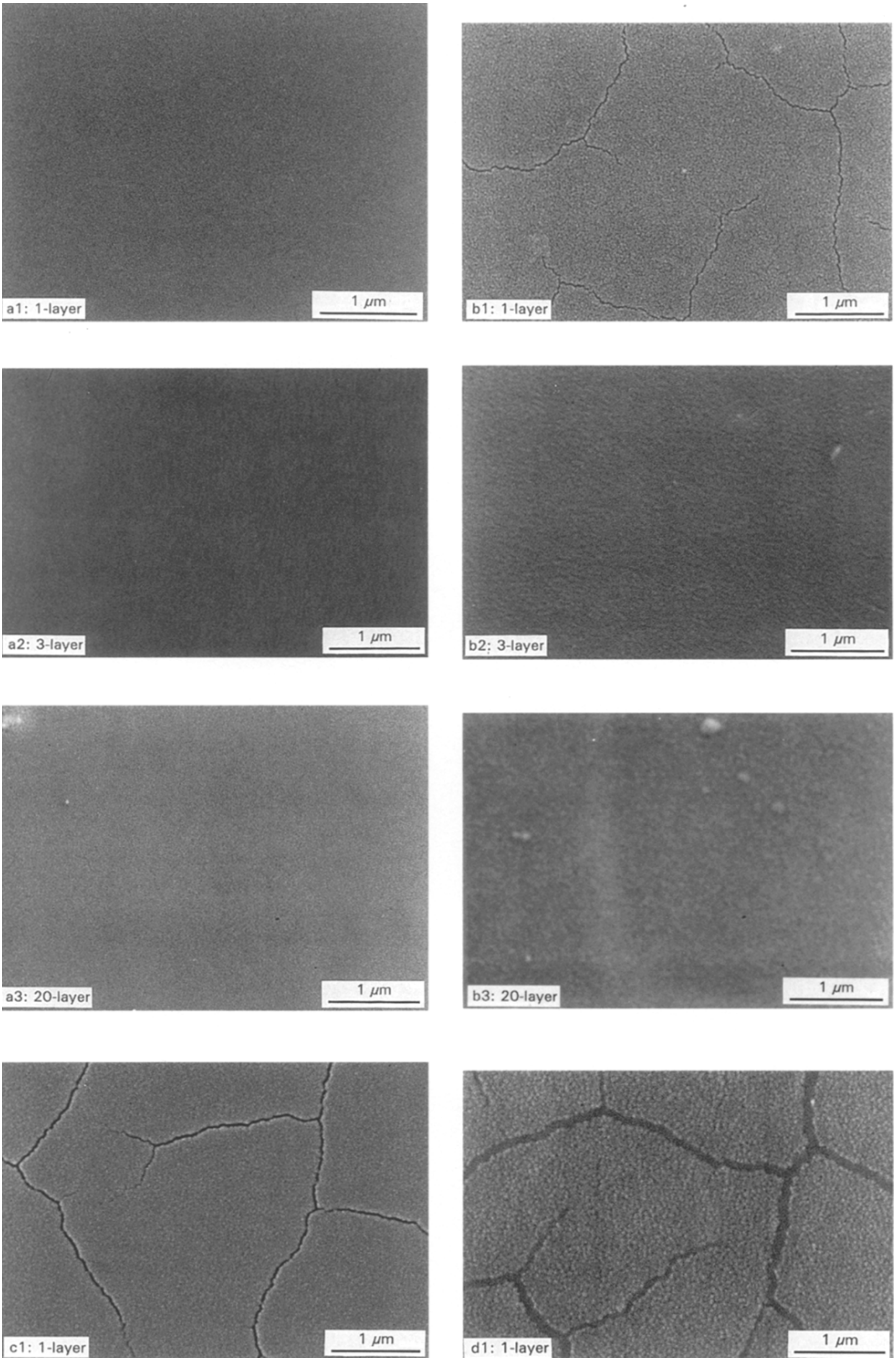
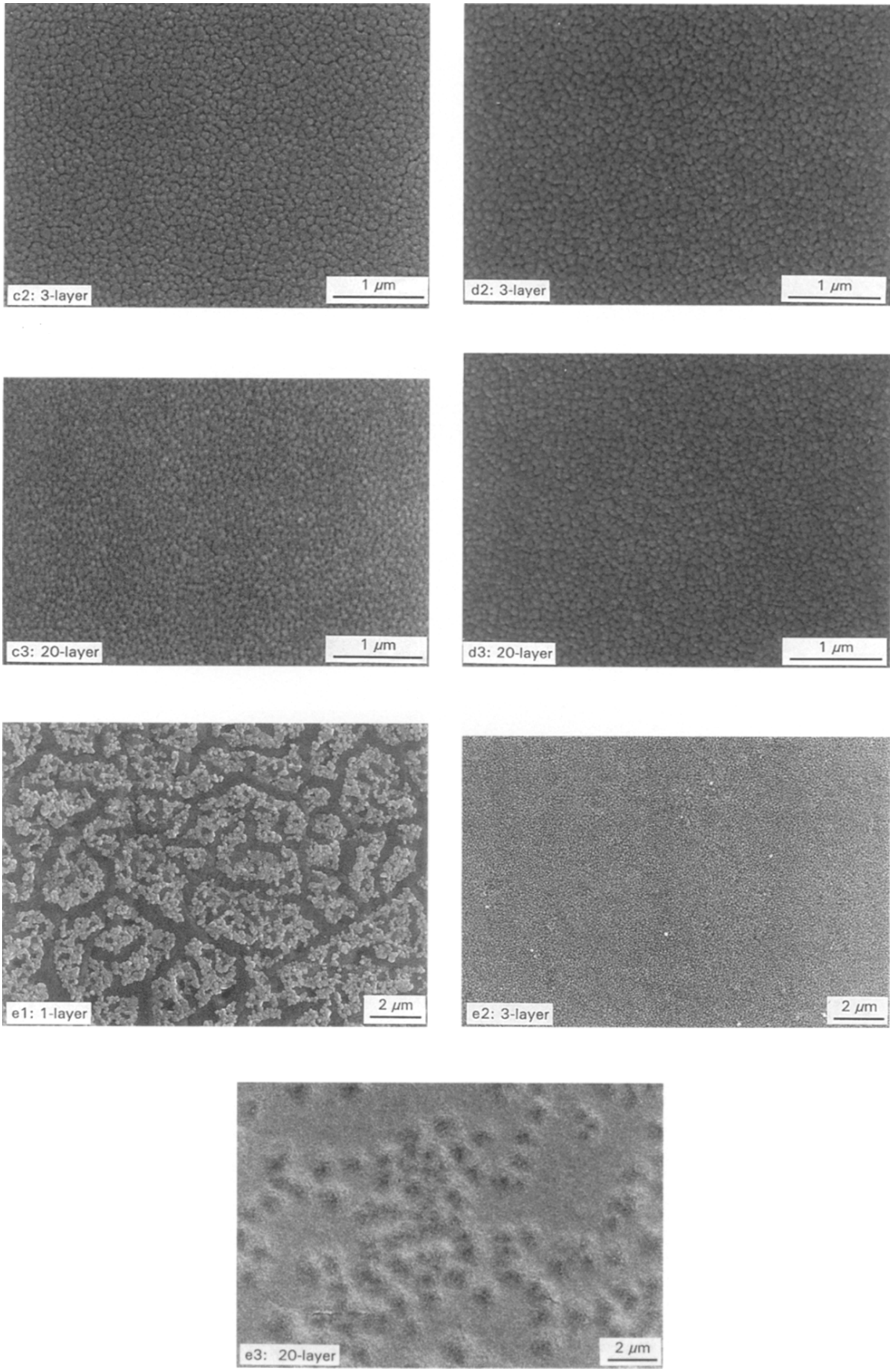


Figure 2 The microstructures of the films after sintering at various temperatures for 1 h: 400 °C (a1, a2 and a3); 900 °C (b1, b2 and b3); 1100 °C (c1, c2 and c3); 1200 °C (d1, d2 and d3) and 1300 °C (e1, e2 and e3).



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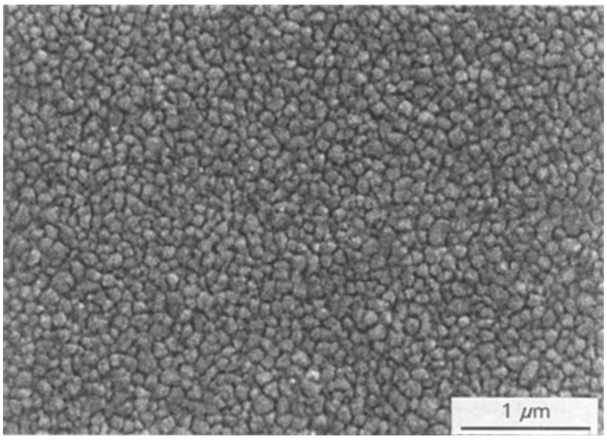

Figure 3 The microstructure of a 20-layer film after sintering at 1200 °C for 20 h.

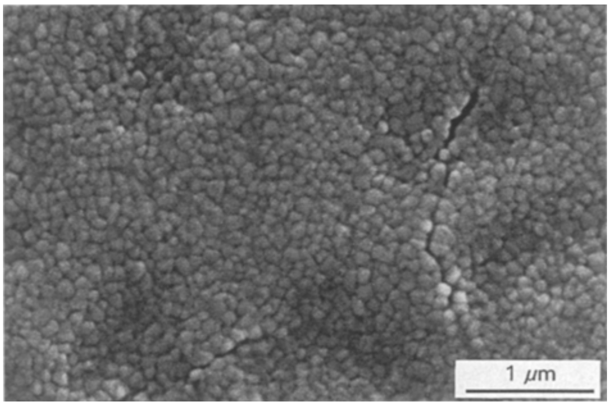

Figure 4 The microstructure of a 20-layer film after sintering at 1300 °C for 1 h.

Fig. 4, pores between the closely packed particles can be identified. Full density had not been achieved.

The above results indicate that after crystallization a film is essentially an assembly of agglomerate-free, uniformly packed nanometre-size grains. The uniformly distributed fine particles and finer pores were maintained and thus no large agglomerates nor large pores were developed at sintering temperatures up to 1200 °C. According to the sintering theory of crystalline ceramics, an ultra-high sinterability may be achieved in the presently studied ceramics because of the extremely favourable kinetics offered by the uniformly distributed nanometre-size grains. However, such an ultra high sinterability was not achieved in all films. Full density was not obtained at sintering temperatures up to 1300 °C. There are two probable causes for the low sinterability obtained in the presently studied gels. First, the green density of a ceramic gel is usually very low, about 25% of the full density. Although the ceramic gel is free of agglomerates and the nanometre grain size offers favourable kinetic conditions for densification, the volume shrinkage required to achieve a full density is so large that the favourable kinetics conditions may have been cancelled by the low green density. By increasing the green density of an agglomerate-free YSZ powder compact, Rhodes [14] obtained a nearly full density at a sintering temperature of 1150 °C. The second cause for the low sinterability may be that the shrinkage of the film is constrained by the substrate, making the film densification difficult. To verify this point, another set of experiments was preformed to study the sintering behaviour of the bulk gels that were not constrained by a substrate.

3.2. The sintering behaviour of YSZ bulk gels

The X-ray diffraction of YSZ bulk gels after sintering at different temperatures is shown in Fig. 5. The bulk gels were still amorphous after sintering at 400 °C for 1 h, but crystallized to a cubic structure on subsequent sintering at 500 °C for 1 h. No further changes in the crystalline structure were detected in samples that were further sintered at 900 and 1300 °C. The fracture surfaces of the bulk samples were examined by SEM. Shown in Fig. 6 (a, b, c, d) are the microstructures of the bulk samples after sintering at 400, 900, 1200 and 1300 °C, respectively. The bulk sample after sintering at 400 °C for 1 h had a very fine and uniform structure; no pores or grains could be clearly identified from SEM observation (Fig. 6(a)). However, on subsequent sintering at 900 °C for 1 h, particles with a diameter of 20–30 nm could be clearly distinguished (Fig. 6(b)). The particles agglomerated together, forming agglomerates of a diameter of approximately 200 nm. Gaps were also appeared between the agglomerates. As the sintering temperature increased to 1200 and 1300 °C, the particles within the agglomerates increased to 50 nm in diameter and the agglomeration of the particles became much more obvious (Fig. 6 (c,d)). Pores of the size of 100–200 nm had now developed between the agglomerates after sintering at 1300 °C. Fig. 7 (a,b)

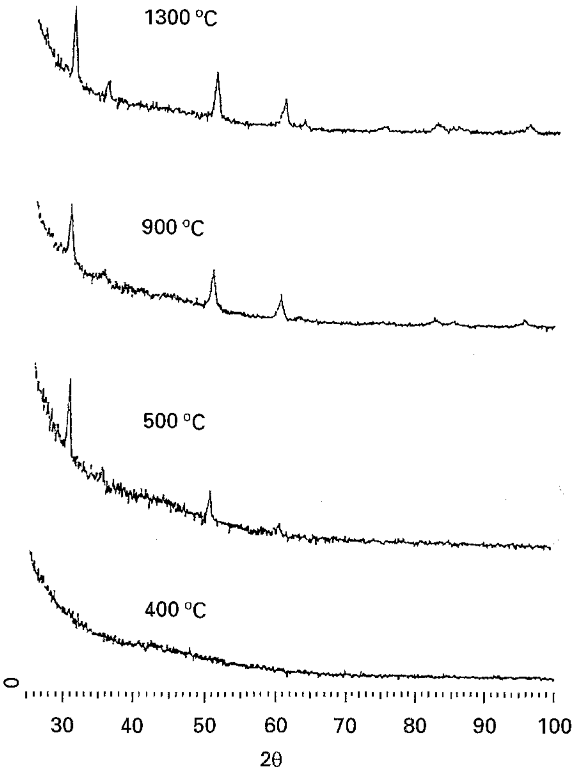

Figure 5 The X-ray diffraction spectra of the YSZ bulk gels after sintering at various temperatures for 1 h.

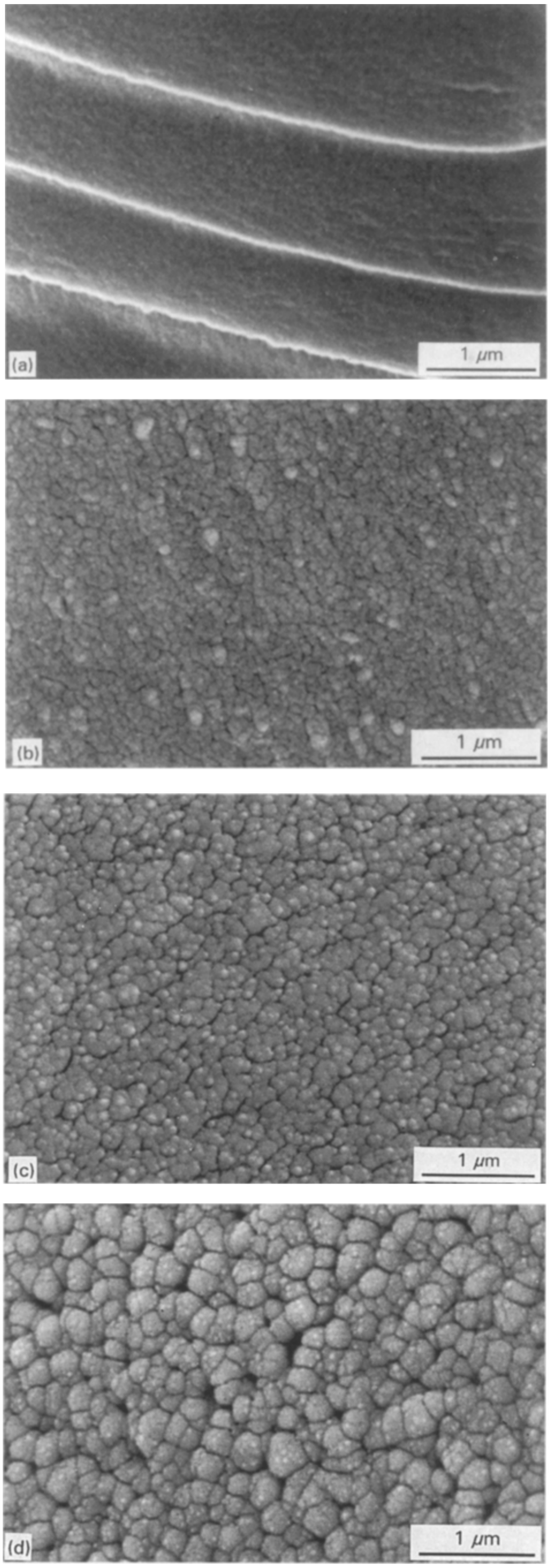

Figure 6 The microstructures of the bulk samples after sintering at various temperatures for 1 h: (a) 400 °C; (b) 900 °C; (c) 1200 °C; (d) 1300 °C.

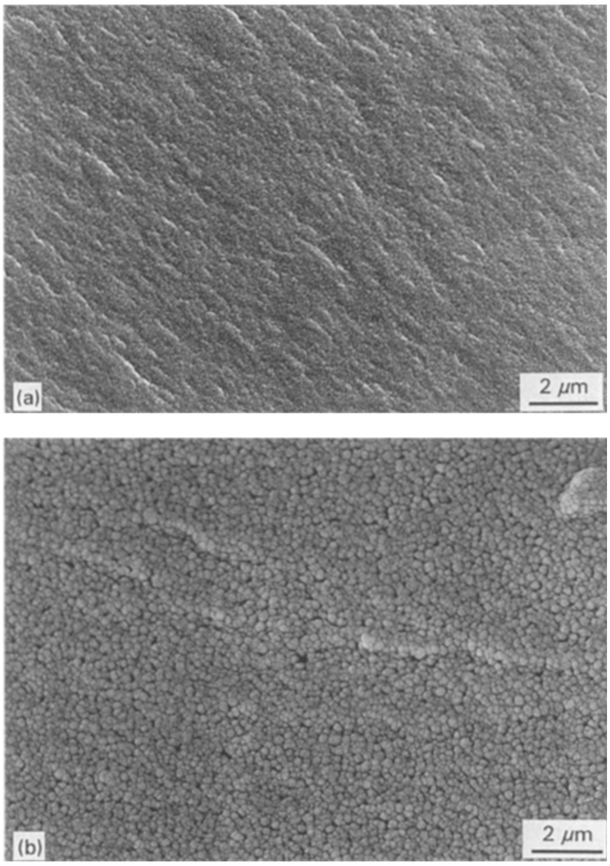

Figure 7 The microstructures of the bulk gels after sintering at 1100 °C (a) and 1300 °C (b) for 1 h.

shows the low-magnification microstructures of the bulk samples sintered at 1100 and 1300 °C, respectively. Clearly, a high density had not been achieved by sintering the bulk gels at 1300 °C for 1 h. Thus, the seemingly dense appearance of the microstructures obtained at sintering temperatures below 1100 °C is because the pores were too fine to be seen. Although the microstructures after 1300 °C sintering were generally very uniform and were free of agglomerates larger than 0.4 µm, agglomerates (or aggregates) did form on a submicrometre scale and led to preferential sintering within the agglomerates on a submicrometre scale.

The experimental results from the bulk gels suggest that the main reason for the low sinterability in both the thin film gels and the bulk gels is not the constraint effect of the substrates on the films, because the bulk gels, without the constraint of a substrate, also exhibited a low sinterability. The poor sinterability observed in the present work is more likely to be caused by the low green density of the dried gels before sintering.

4. Summary

The initially dried gels (both thin film and bulk) were seemingly dense and were free of pores larger than 30 nm. The gels crystallized between 400 and 500 °C, and the crystallized gels were essentially an assembly of uniformly packed nanometre size grains. As the sintering temperatures increased, the nanometre-size grains started to sinter together, forming larger aggregates (or agglomerates). As a result of the formation of the aggregates, pores between the aggregates increased in size due to the preferential intra-aggregate sintering over the inter-aggregate sintering. The sintering at 1300 °C led to a significant shrinkage in the films that had been previously sintered at 1200 °C. As a result of the large shrinkage, all of the films cracked. Voids were also formed in the 20-layer film. However, up to the sintering temperatures of 1200 °C, the 3- and 20-layer YSZ films maintained a uniform distribution of fine particles and fine pores, with average diameters of less than 100 nm.

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