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Adsorption of polyvinylpyrrolidone (PVP) and its effect on the consolidation of suspensions of nanocrystalline CeO_2 particles

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CeO_2 particles with an average size of ~9 nm were synthesized under hydrothermal conditions. The adsorption of polyvinylpyrrolidone (PVP) on to the particle surfaces was measured in aqueous suspensions in the pH range of ~3.7 to 11.5. The amount of adsorbed PVP decreased significantly with increasing pH value. For suspensions prepared at a pH value of ~3.7, complete adsorption occurred for ~2.5 wt % of PVP added to the suspension. Further additions of PVP produced a gradual increase in the adsorption until a limiting value was reached when the total amount of PVP added to the suspension was 10 wt %. At this PVP concentration, ~6 wt % of the PVP was adsorbed and ~4 wt % remained free in solution. The effect of the adsorbed PVP on the microstructural homogeneity of films deposited by spin coating of suspensions was investigated. With no addition of PVP, crack-like voids were prevalent in the dried and sintered films. Crack-free films were obtained from suspensions containing 10 wt % of PVP. Higher PVP additions (25 wt %) produced an increase in the viscosity of the suspension but no observable change in the microstructural homogeneity of the films. The use of adsorbed polymers for steric stabilization coupled with data from the adsorption isotherms is shown to provide a rational approach to the deposition of homogeneous films from suspensions of nanocrystalline particles. © *1999 Kluwer Academic Publishers*

1. Introduction

Suspensions of nanocrystalline particles (particle size less than ~50 nm) can provide significant advantages for the production of porous and dense films for several technological applications, including membranes for gas and liquid separation and electrolytes in solid oxide fuel cells [1]. They allow the formation of films with thickness in the range of a fraction of a μm to a few μm which cannot be achieved with coarser powders. The achievement of relatively high porosity and fine pore sizes in porous films is also significant. For dense films, the enhanced sinterability associated with the fine particle size provides the advantage of lower temperature fabrication. However, the fine size of the nanocrystalline particles can present problems in the consolidation of the suspension.

For good homogeneity of the deposited film, suspensions with good stability against flocculation and with a relatively high concentration of particles are required to reduce differential shrinkage during drying and sintering. In earlier work by Yang and Rahaman [2], it was observed that in the case of electrostatically stabilized suspensions, good stability was achieved for dilute suspensions of nanocrystalline CeO_2 particles. However, an increase in the particle concentration produced considerable flocculation. Films produced from the electrostatically stabilized suspensions with the higher particle concentration were fairly inhomogeneous. The addition of PVP was found to significantly improve the stability of the suspensions and the homogeneity of the films. Crack-free films with a uniform thickness were obtained by spin coating followed by sintering.

The work described in the present paper formed an extension of the earlier work of Yang and Rahaman [2] to investigate the adsorption behavior of polymeric additives onto the CeO_2 particle surfaces and to relate the adsorption data to the microstructure of the deposited films. The adsorption isotherms for PVP in suspensions of nanocrystalline CeO_2 were measured at different pH values. Suspensions containing polymer concentrations at selected positions on the adsorption isotherms were prepared and used for the deposition of films by spin coating. The microstructure of the dried films and the sintered films were observed by scanning electron microscopy.

2. Experimental

Nanocrystalline CeO_2 particles were synthesized by precipitation from solution under hydrothermal conditions, as described in detail elsewhere [2–4]. A

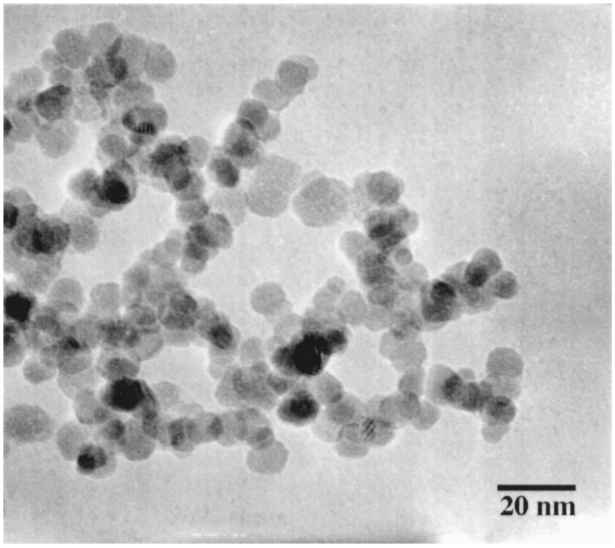

Figure 1 TEM micrograph of the nanocrystalline CeO_2 particles used in the experiments.

transmission electron micrograph of the particles is shown in Fig. 1. Analysis by X-ray line broadening showed that the particles were crystalline with an average size of ∼9 nm.

After the synthesis step, the particles were washed with distilled water, collected in a centrifuge and dispersed in a known volume of distilled water. Suspensions with a given concentration of particles were obtained by the addition or evaporation of water. In this way, the particles used in the subsequent adsorption experiments did not undergo a drying step. The formation of strong agglomerates of primary particles, commonly found in dried particulate systems, was therefore avoided.

The adsorption behavior of PVP (molecular weight ≈30,000) and polyethylene glycol (molecular weight ≈40,000) on to the CeO_2 particle surfaces was investigated. However, the polyethylene glycol did not show any significant adsorption onto the particle surfaces and only the experiments with PVP will be described here. In the experiments, 50 cm^3 of the suspension with a particle concentration of 0.025 g/cm^3 (0.35 vol %) was prepared at the required pH value (∼3.7, 8.1 and 11.5) by the addition of a few drops of HNO_3 or NH_4OH solution followed by stirring for 30 min. To control the accuracy of the PVP concentration in the suspension, PVP was added in the form of a solution. A given amount of PVP was dissolved in 100 cm^3 of distilled water and 10 cm^3 of the solution was added to the suspension. The mixture was stirred at room temperature for 24 h for adsorption to take place. The particles were then collected in a centrifuge (Sorvall Instruments RC5C; DuPont Co., Wilmington, DE, USA) and washed three times with distilled water, followed by centrifugation, to remove the unadsorbed polymer molecules. The powder was dried at 80 °C for 48 h.

The mass of adsorbed PVP on the particle surfaces was measured by thermogravimetric analysis, TGA (TA1; Mettler Instruments, USA) using a heating rate of 10 °C/min to 800 °C. For comparison, the CeO_2 powder without any adsorbed polymer was analyzed under the same conditions. The data were considered in terms of the mass of PVP adsorbed per unit area of the CeO_2 powder as a function of the total amount of PVP added to the suspension. The surface area of the powder was determined from the mass of the powder, the theoretical density of CeO_2 (assumed to be 7.0 g/cm^3), the average particle size of the powder (9 nm) and by making the approximation that the particles were spherical in shape. The amount of PVP added to the suspension was expressed as a fraction of the dry mass of the powder (sometimes referred to as a *dry weight basis*, dwb).

Suspensions of the nanocrystalline CeO_2 particle were used to prepare films by spin coating (Model CEE-100CB, Brewer Science, Inc., Missouri, USA) to determine qualitatively the influence of the adsorbed polymer on the consolidated microstructure. The suspensions were prepared with a fixed concentration of particles (10 vol %) and at a pH value of ∼3.7 that provided the least tendency for flocculation. Suspensions containing 0, 10 and 25 wt % of PVP were used. The suspensions were stirred for 24 h under the conditions described earlier for the adsorption experiments. In the spin coating experiments, ∼0.2 cm^3 of the suspension was placed on a ZrO_2 substrate and the system was accelerated rapidly to a speed of 1,000 rev/min. After 45 s, the coated substrate was removed and dried for 24 h at 70 °C. The films were heated in air at 1 °C/min to 400 °C to burn off the polymeric material and then sintered at 10 °C/min to 1350 °C to achieve densification. The microstructure of the top surface of the films was observed using scanning electron microscopy (SEM).

3. Results and discussion

Fig. 2 shows the adsorption isotherms for PVP on the nanocrystalline CeO_2 particles for suspensions prepared at three pH values of 3.7, 8.1 and 11.5. For comparison, the diagonal line shows the adsorption behavior that would occur if 100% of the PVP added to the

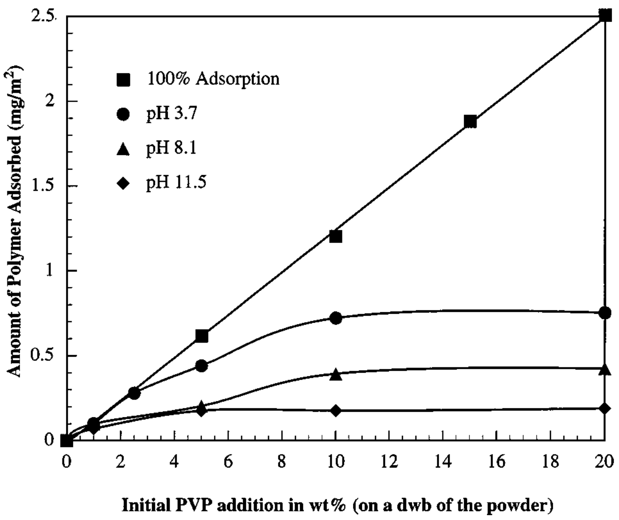

Figure 2 Adsorption isotherms for PVP on to nanocrystalline CeO_2 particles in aqueous suspensions at pH values of 3.7, 8.1 and 11.5.

solution were to adsorb. The amount of adsorbed polymer is seen to decrease significantly with increasing pH value of the suspension. The isoelectric point for CeO_2 was determined to be in the pH range of 5–6. The particle surfaces are positively charged below the isoelectric point whereas they are negatively charged above the isoelectric point. For any pH value, all of the PVP initially added to the solution is adsorbed on to the particle surfaces after which there is a gradual attainment of the adsorption plateau. At the pH value of 11.5 (i.e., above the isoelectric point), the adsorption plateau is reached after the addition of only ∼1 wt % of PVP to the suspension. At the pH value of 3.7 (i.e., below the isoelectric point), 100% adsorption occurs for ∼2.5 wt % of PVP added to the suspension and the amount of adsorbed polymer gradually increases with further additions of PVP, reaching a plateau region after the addition of 10 wt % PVP. At this PVP concentration, ∼6 wt % of the PVP is adsorbed and ∼4 wt % remains free in solution. Using the surface area determined from the average size of the particles, the amount of adsorbed polymer corresponds to a surface coverage on the particles of ~ 0.75 mg/m^2.

For a given mass of polymer adsorbed per unit area of the particle surface and assuming the same polymer configuration on the particle surface, the total amount of polymer that must be added to the suspension increases inversely with the radius of the particles. For good stability, suspensions of nanocrystalline particles may therefore be expected to contain considerably higher concentrations of polymeric stabilizers when compared to similar suspensions of micron-sized particles. As outlined above, for the suspensions of nanocrystalline particles investigated in this work (pH value = 3.7), ∼10 wt % of PVP is required to reach the adsorption plateau. For micron-sized particles, the data in the literature indicate that the amount of polymeric dispersant required to obtain relatively stable suspensions is commonly a fraction of a wt % [5, 6].

The effect of the PVP concentration on the consolidated state was investigated for films prepared by spin coating of the suspensions at a pH value of 3.7. The concentrations of PVP in the suspensions corresponded to representative points on the adsorption isotherm shown in Fig. 2. They consisted of 0 wt % (no addition of PVP), 10 wt % (the onset of the adsorption plateau) and 25 wt % (significantly far along the adsorption plateau). Fig. 3 shows SEM micrographs of the top surfaces of films deposited from suspensions. The suspension containing no PVP achieves its stability through electrostatic repulsion between the positively charged particle surfaces. On consolidation, the film is seen to contain a large number of crack-like flaws (Fig. 3a). For the suspension containing 10 wt % PVP, the significant amount of adsorbed polymer (6 wt %) is expected to provide a high degree of steric stabilization. However, there is also a significant amount (4 wt %) of free polymer in solution which would increase the viscosity of the liquid. The film prepared from the suspension with 10 wt % PVP appears relatively smooth and shows no evidence for the presence of crack-like flaws (Fig. 3b). When the PVP concentration is increased to 25 wt %, the additional polymer essentially goes wholly into solution and serves to increase the viscosity of the liquid. Films deposited from the suspension (Fig. 3c) appear to be qualitatively similar to those deposited from the suspension with 10 wt % PVP.

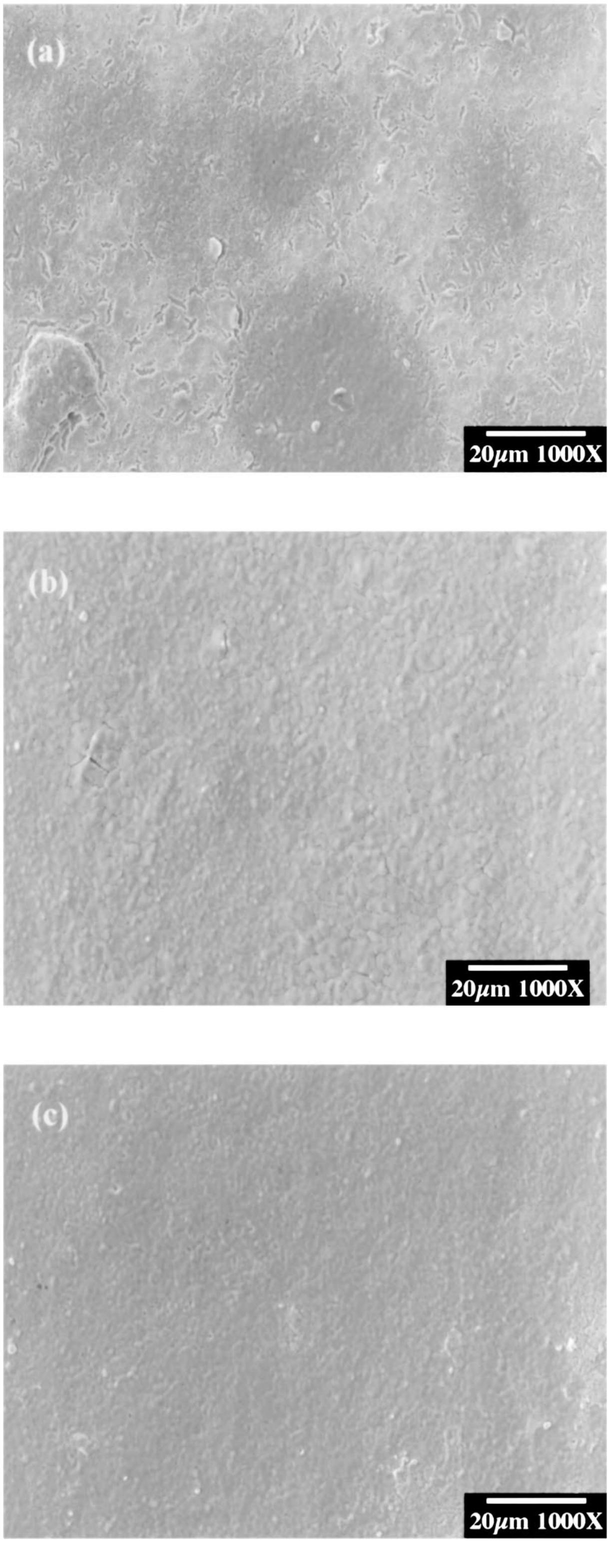

Figure 3 SEM micrographs of the top surfaces of the films prepared by spin coating of CeO_2 suspensions at a pH of 3.7 and containing (a) 0, (b) 10 and (c) 25 wt % PVP.

Fig. 4 shows SEM micrographs of the top surfaces of the films after sintering to 1350 °C. Crack-like voids are prevalent in the film formed from the suspension containing no PVP. The films prepared from the suspensions with 10 and 25 wt % PVP appear to be very dense. As with the unfired films, the increase in the PVP concentration from 10 to 25 wt % does not appear to provide any benefits in the microstructure of the sintered films. However, a disadvantage of the use of the higher PVP concentration is the removal of a significant volume fraction of polymer from the film prior to sintering.

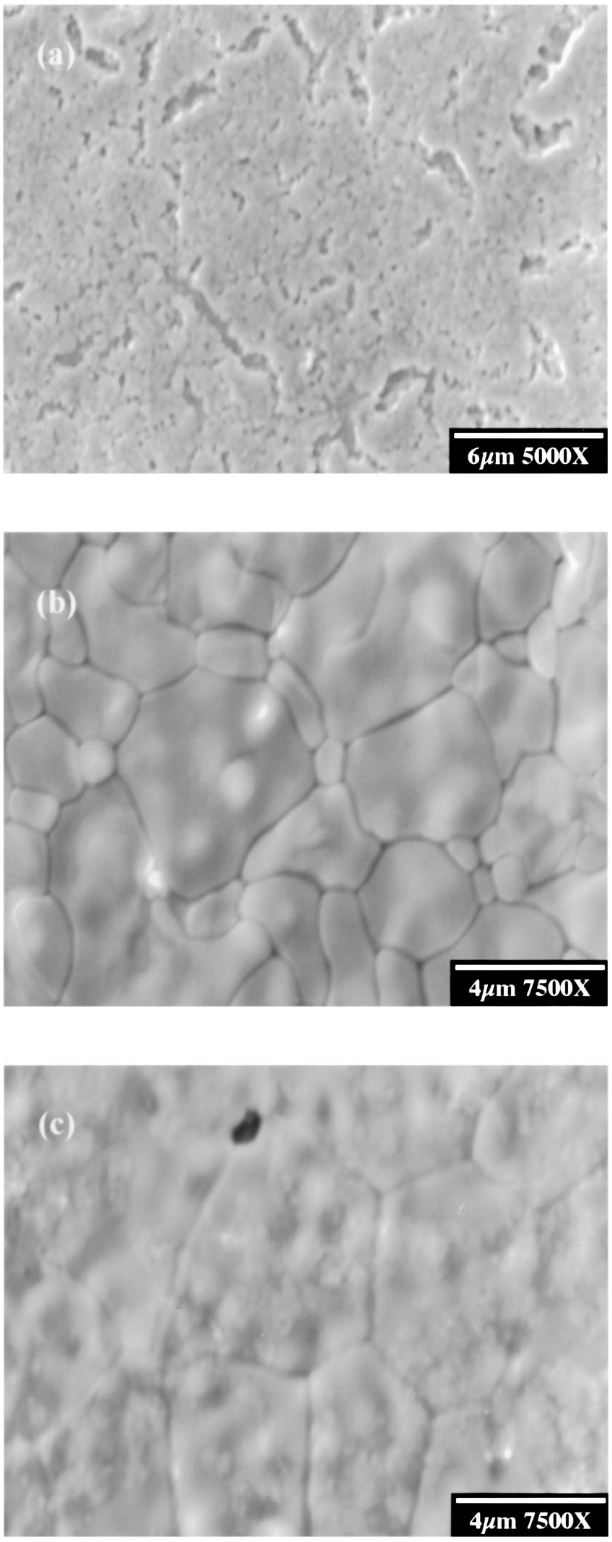

Figure 4 SEM micrographs of the top surfaces of the CeO_2 films shown in Fig. 3 after sintering at 10 °C/min to 1350 °C. The films were prepared from suspensions at a pH of 3.7 and containing (a) 0, (b) 10 and (c) 25 wt % PVP.

4. Conclusions

For aqueous suspensions with pH values in the range of 3.7–11.5, the adsorption of PVP on to the surfaces of nanocrystalline CeO_2 particles decreased with increasing pH. At the pH value of 3.7, 100% adsorption occurred for $\sim$2.5 wt % of PVP added to the suspension and the amount of adsorbed polymer gradually increases with further additions of PVP, reaching a limiting value of $\sim$0.75 mg/m^2 at a PVP concentration of $\sim$10 wt %. At this PVP concentration, $\sim$6 wt % is adsorbed and $\sim$4 wt % remains free in solution. Films deposited by spin coating from the suspension containing no PVP developed crack-like voids after drying and sintering. In contrast, films deposited from the suspension containing a PVP concentration at the onset of the plateau region of the adsorption isotherm (10 wt %) were crack-free under nearly identical drying and sintering conditions. Films deposited from suspensions with much higher PVP concentration (25 wt %) appeared to be qualitatively similar to those with 10 wt % PVP.

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