Journal of the European Ceramic Society **14** (1994) 337–341

Solute Effect on Grain Growth in Ceria Ceramics

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(Received 25 October 1993; accepted 5 April 1994)

Abstract

In the present work the preparation of CeO_2 ceramics doped with Y_2O_3 (0–10 mol%) following the conventional mechanical mixing and solid state reaction of constituent oxides is described. Compositions were calcined at 1500°C for 3 h for solution formation and finely ground to maintain the average particle size at 0·5 μm in all cases. Characterization at different stages was performed for chemical composition, solid solution formation, powder particle size distribution and specific surface area. Densification behaviour was studied by high temperature dilatometry. Samples of near theoretical density were obtained by sintering at 1600°C for 6 h. Microstructural analysis showed a fine grain size (e.g. ~15 μm for 1·0 mol% Y_2O_3 compositions), having a narrow size distribution and an intergranular porosity. An inverse dependence of grain size on solute content was observed, suggesting the role of yttria as a grain growth inhibitor for the CeO_2 matrix. This correlation has been explained on the basis of the currently accepted model of space charge induced grain boundary segregation of the solute ions.

In der vorliegenden Arbeit wird die Herstellung von CeO_2-Keramiken, die mit Y_2O_3 (0–10 mol%) dotiert sind, über das übliche mechanische Mischen und eine Festkörperreaktion der Oxide beschrieben. Die Zusammensetzungen wurden bei 1500°C drei Stunden lang kalziniert, um eine Lösung zu bilden, und anschließend gemahlen, um eine durchschnittliche Teilchengröße von 0·5 μm beizubehalten. In verschiedenen Stadien wurden die Zusammensetzungen in Hinsicht auf chemische Zusammensetzung, Mischkristallbildung, Pulverteilchengrößenverteilung und spezifische Oberfläche charakterisiert. Das Verdichtungsverhalten wurde mit Hilfe der Hochtemperatur-Dilatometrie untersucht. Proben mit nahezu theoretischer Dichte wurden durch Sintern bei 1600°C für sechs Stunden erhalten. Mikrostrukturuntersuchungen zeigten eine kleine Korngröße (z.B. ~1·5 μm für Zusammensetzungen mit 1·0 mol% Y_2O_3) mit enger Größenverteilung und intergranularer Porosität. Eine reziproke Abhängigkeit der Korngröße vom Dotierungsgehalt wurde beobachtet, was nahelegt, daß Y_2O_3 als Kornwachstumshemmer für die CeO_2-Matrix wirkt. Diese Beziehung wurde auf der Basis des momentan akzeptierten Modells der durch Raumladung verursachten Korngrenzense-gregation der Dotierungsionen.

On Décrit dans cet article la préparation de céramiques à base de CeO_2 dopées avec Y_2O_3 (0–10 mol%) per mélange mécanique conventionel et par réaction des oxides en phase solide. Les différents échantillons ont été calcinés à 1500°C pendant 3 h pour permettre la formation de solutions solides et finement broyé pour maintenir une taille moyenne de grains de 0·5 μm. On a mesuré à différents stades la composition chimique, la formation de solutions solides, la taille des particules de poudre et la surface spécifique. L'évolution de la densité a été étudiée par dilatométrie à haute température. Des échantillons avec pratiquement une densité théorique ont été obtenus par frittage à 1600°C pendant 6 h. L'analyse microstructurale montre une faible taille des grains (~15 μm pour une composition avec 1·0 mol% de Y_2O_3) ainsi qu'une fine distribution de celle-ci, et une porosité intergranulaire. On a observé que la taille des grains était inversement proportionelle à la teneur en soluté, ce qui suggère que l'oxide d'yttrium inhibe la croissance des grains d'une matrice de CeO_2. Cette corrélation est expliquée sur la base du modèle couramment accepté de la ségrégation des ions du soluté aux joints de grains induie par les charges.

Journal of the European Ceramic Society 0955-2219/94/$7.00

1 Introduction

The fluorite structure oxides, viz. ZrO_2, CeO_2 and ThO_2, have important structural, electrochemical and nuclear applications. When doped with lower valence cations, these oxides behave as good ionic conductors at elevated temperatures, due to the introduction of oxygen ion vacancies as charge-compensating lattice defects for the substituted cations. Zirconia ceramics are widely used for oxygen monitoring and controlling of various combustion processes.[1,2]

Cerium oxide based solid solutions have many desirable characteristics for ceramic solid electrolyte applications. In the pure form CeO_2 has been established as a promising material for the newer generation of resistive-type oxygen sensors.[3] Doped ceria exhibits higher oxygen ion conductivity than zirconia for the same solute concentration.[4–6] Specifically, the yttria-doped ceria ceramics serve as a model defect fluorite system allowing the analysis of various point defect interactions influencing the ionic conductivity due to the presence of a single-phase field over a wide range of compositions. The charge transport properties are primarily controlled by the concentration and the size factor of the solute. The microstructural design features also have an important bearing with respect to the volume fraction of the grain boundary phase and its chemistry.[7,8] The latter is mostly due to impurity pickup during processing, while the former results from the grain boundary drag factor in the presence of dopant. The present work analyses these features in the case of CeO_2–Y_2O_3 solid solutions in the dilute range which is of most practical interest.

2 Experimental

Ceria ceramics containing yttria in the dilute composition range of 0–10 mol% in steps of 1 mol% were investigated. The starting materials were nominally 99·95% pure CeO_2 and Y_2O_3. Appropriate amounts of these oxides were mechanically mixed and different batch mixtures were calcined at 1500°C for 3 h using alumina boats. The hard calcined mass was crushed in a pestle and mortar to less than 75 μm and then subjected to extensive attrition milling. The mill contained a polyamide jar, Y-TZP grinding balls and isopropyl alcohol as the dispersing medium. The slurries were dried in an air oven and finally granulated by sieving. Powders were characterized for chemical composition (AAS), specific surface area (BET–N_2 adsorption) and particle size distribution (sedimentation). Cold compacted samples were sintered at 1500°C and 1600°C for 6 h to study the densification behaviour. Bulk density was measured by liquid displacement method. The shrinkage behaviour of powders was analysed using dilatometry technique. For this purpose the samples (10 mm height × 6 mm diameter) were prepared by CIP at 630 MPa without any binder. The solid solution formation and consequent change in lattice parameter was estimated by XRD. Microstructural features were studied by optical and scanning electron microscopes on polished and thermally etched samples.

3 Results and discussion

3.1 Solid solution formation

Ceria, being a refractory oxide, needs high processing temperatures. The intimate admixture of constituent oxides were thus calcined at 1500°C in order for the diffusion process to complete within a reasonable time. Generally, an equilibration time exceeding about an hour at 1500°C was found to be sufficient for homogenization. This was confirmed by XRD, as shown in Fig. 1. Only the relevant reflections for the fluorite phase are present for CeO_2–3·0 mol% Y_2O_3 samples. For sinter activity the calcined product was converted into the form of fine powder. Analysis for the mean and the net size range of the powder particles was performed. A representative plot for CeO_2–3·0 mol% Y_2O_3 powder is shown in Fig. 2. An appreciably monomodal distribution of powder particles was obtained with a median size around 0·5 μm, for all the compositions. There was no perceptible influence of solute content on the comminution behaviour of ceria on milling under

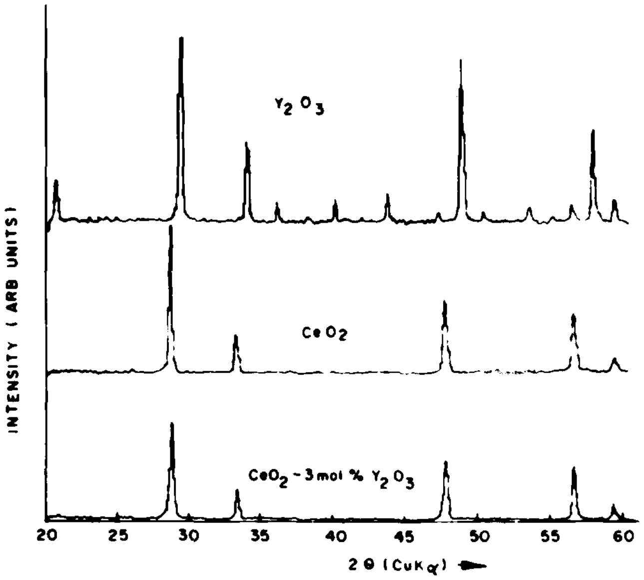

Fig. 1. XRD profiles indicating the formation of yttria-doped ceria ceramics.

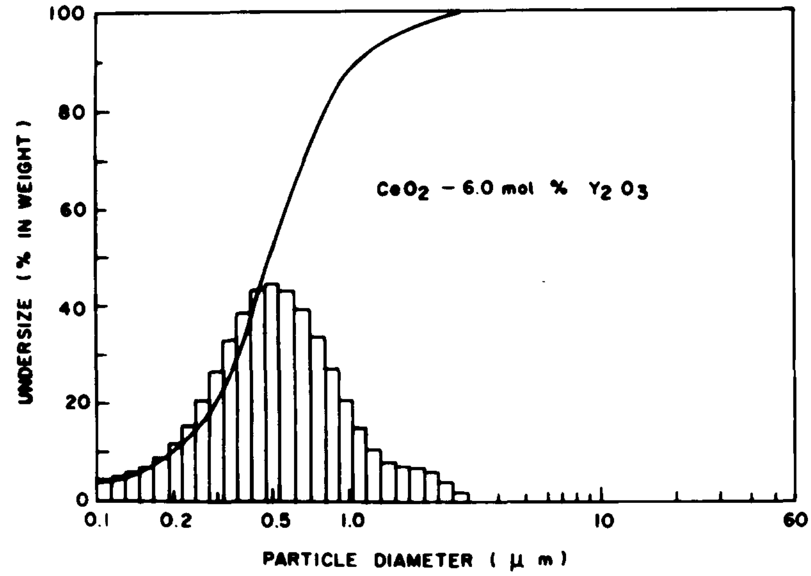

Fig. 2. Particle size distribution of attrition milled CeO_2–Y_2O_3 powder.

identical conditions. The BET specific surface area was also found to be within ±10% of the mean value of 6·5 m^2 g^{-1} for these powders. Excellent compactibility was observed, yielding relative green density of 55–58% at 630 MPa. This is due to the efficient milling conditions used which produces a fine dispersion and agglomerate-free powders.

Dilatometry results are presented in Fig. 3 for CeO_2–8·0 mol% Y_2O_3. It shows a uniform densification curve, with a macroscopic shrinkage onset temperature of 900°C, inflection point at ~1200°C and process completion at 1500°C. Based on these results the isothermal sintering was carried out at 1500°C and 1600°C for 6 h, which resulted in impervious and high density samples. As an example, for CeO_2 containing up to 3 mol% Y_2O_3, the bulk density achieved was 98% and 99% of the theoretical value when sintered at 1500°C and 1600°C respectively. However, for a higher solute content, a slight lowering of density was observed.

3.2 Solute effect on microstructure

Microstructure evolution in CeO_2–Y_2O_3 solid solutions after high temperature sintering is presented in Fig. 4 in the form of selected micrographs. To delineate the grain boundaries the polished samples have been subjected to thermal etching treatment. Fig. 4(a,b,c) presents the optical micrographs for the 1500°C sintered samples of CeO_2 containing 1·0, 3·0 and 6·0 mol% Y_2O_3 respectively. The effect of raising the firing temperature by 100°C on microstructural features is revealed in Fig. 4 (d,e,f). These are the SEM results on the corresponding samples included for comparison. The general features in Fig. 4(a–f) are identical. A single-phase dense matrix with a homogeneous microstructure is obtained. Important characteristics observed are:

(a) Equiaxed and ultrafine grains with a reasonably narrow size distribution.

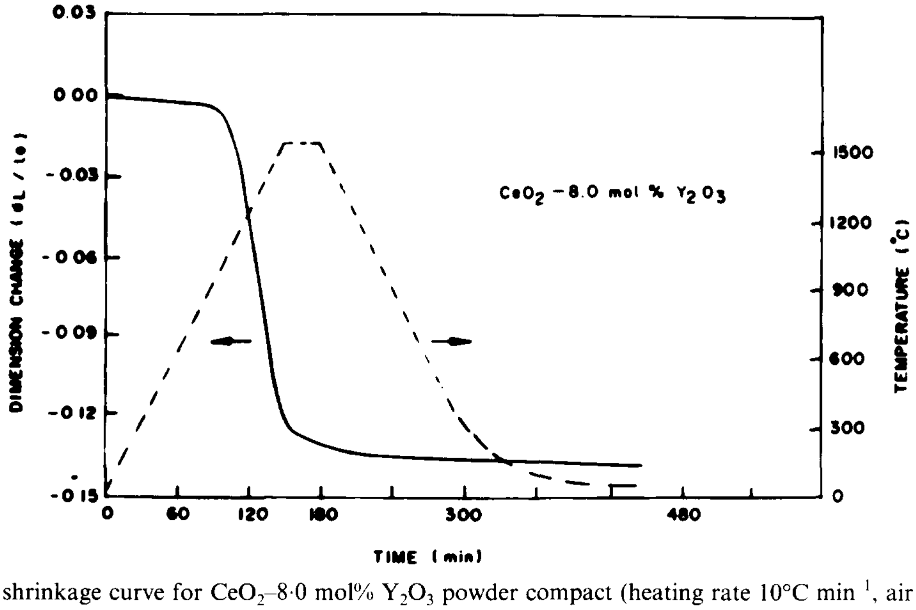

Fig. 3. Linear shrinkage curve for CeO_2–8·0 mol% Y_2O_3 powder compact (heating rate 10°C min^{-1}, air atmosphere).

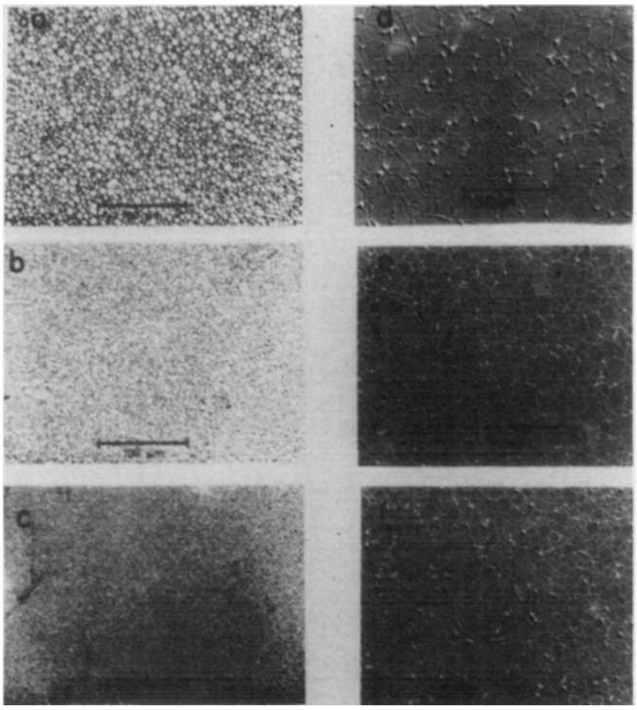

Fig. 4. Microstructural variations in ceria ceramics as a function of solute concentration and sintering temperature. Micrographs a, b and c are for samples sintered at 1500°C containing 1·0, 3·0 and 6·0 mol% Y_2O_3 respectively and d, e, and f correspond to 1600°C sintering treatment.

(b) The grain size parameter shows an inverse dependence on the solute content.

(c) The porosity is fine (0·3 μm), monosized and predominantly intergranular.

A minor entrapped porosity fraction was completely eliminated with increasing Y_2O_3 concentration. A quantitative estimate of grain size was made on the micrographs by the linear intercept method. Figure 5 thus shows the grain size dependence of CeO_2 ceramics on the concentration of Y_2O_3 in the range of the present investigations. Yttria helps in maintaining the (ultra)fine grain structure which is stable against coarsening during sintering. The grain size increases by a factor of ~1·5 on raising the sintering temperature (to 1600°C).

Evidently the role of Y_2O_3 is to suppress the grain boundary mobility and retard the kinetics of mass transport during sintering. This inhibition effect can be satisfactorily rationalized on the basis of the 'space charge' model, accounting for the solute drag effect.[9–11] Considering the CeO_2–Y_2O_3 alloying, the defect reaction can be written as:

$$Y_2O_3 \xrightarrow{CeO_2} 2Y'_{Ce} + V_O^{\cdot\cdot} + 3O_O^{x} \qquad (1)$$

The symbols have their usual significance in the Kröger and Vink notations. It shows that one oxygen vacancy is formed for every two Y ions for charge compensation. By attractive interaction among the oppositely charged point defects, the $(Y'_{Ce}–V_O^{\cdot\cdot})^{\cdot}$ pairs are formed, leaving Y'_{Ce} ions distributed elsewhere in the lattice.[12–14]

According to the space charge concept, if the Y solute with an effective negative charge is present in the bulk of the grain, then the surface in equilibrium must possess a countercharge which is positive. The dopant in turn by Coulumb attraction segregates to the region adjacent to the surface as a space charge (so that the charge neutrality is maintained for the bulk of the material). This implies the presence of an enrichment layer of solute (and impurity) ions at grain boundaries. The excess localized Y solute thus generates a steeper gradient between bulk and intergrain interfaces. Consequently the solute gradient offers a stronger drag to the boundary mobility, resulting in an effective retardation of grain growth. Direct experimental evidence for such a solute segregation phenomenon in several oxide systems has been obtained by various electronic optical techniques (ESCA, AES and STEM)[10,11] In 3Y-TZP, the enrichment ratio was found to be around 1·9 after sintering at 1400°C. For MgO-doped Al_2O_3, the change in microhardness profiles at the grain boundary was also attributed to the segregation of the dopant. As seen in Fig. 5, for CeO_2–Y_2O_3, the inhibition effect is very prominent in the dilute alloying range (up to 3·0 mol%), where the Y'_{Ce} ions are in noninteracting configurations.

At higher concentrations a clustering of the Y ions and formation of larger complexes of $V_O^{\cdot\cdot}$ and Y'_{Ce} is expected. Furthermore, the difference in solute and solvent atom size (0·102 nm and 0·097 nm respectively) causes a local distortion of the lattice. This strain energy component and the

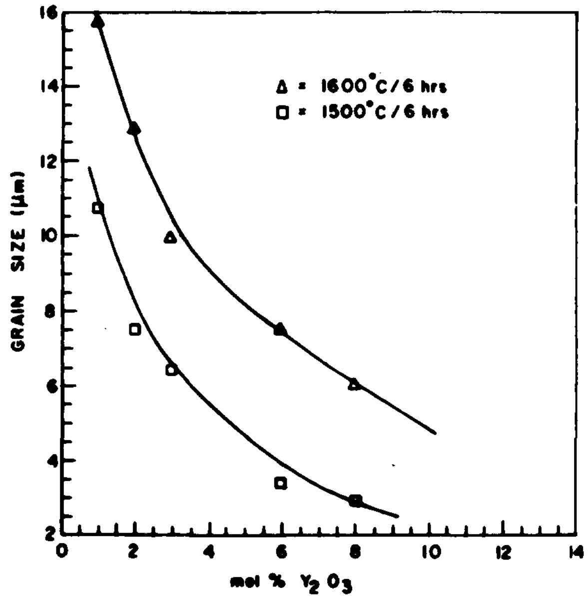

Fig. 5. Solute effect on grain growth of ceria ceramics. Yttria was observed to inhibit the grain growth considerably.

defect agglomerates slow down the ionic mobility. The slight decrease in density for high Y_2O_3 compositions can thus be attributed to the above two rate-controlling factors.

4 Conclusions

(1) This study establishes a useful flow sheet for the preparation of dense yttria-doped ceria ceramics, using conventional ceramic processing. Such ceramics have potential application as solid electrolytes involving oxygen ion conduction.

(2) The grain size bears an inverse dependence to the solute concentration. This is because of the reduced boundary mobility caused by the segregation of dopant cations at the grain boundaries.

(3) Y_2O_3-doped CeO_2 possesses a positively charged grain boundary region due to various point defect interactions. This leads to an effective negative space charge of Y^{3+} solute and its consequential enrichment of the grain boundaries.

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