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Ca-PSZ prepared via polymeric sol–gel route

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Abstract

Microstructural control of 10 mol% Ca-PSZ through doping and heat treatment was studied after firing at 1300, 1400 and 1500°C/2 h using SEM. Tetragonal precipitate was developed under a condition of metastability and transformed partially to monoclinic in the presence of stresses developed through nucleation and growth when the particle size became above the critical grain size. The volume of critically metastable t-precipitate was maximized to more than 90% through controlling transformation between 1300 and 1400°C/2 h. The average grain size of the major phase is related to the precipitation conditions, where t-ZrO_2 precipitate prevents abnormal grain growth and swallows pores. Combined with submicron size microstructure, closed packing without any signs of pores exists without applied stress at 1400°C/2 h. Controlled chemical preparation via polymerization reaction of urea with formaldehyde forming polyamide resin was utilized for preparation of very fine nanomaterials with narrow particle size distribution. Metal cations are homogeneously distributed through the structure of the resin. The conditions achieved lead to the precipitation of tetragonal zirconia without grain growth or crack formation.

Keywords: Ca-PSZ preparation; Polymeric sol–gel route

1. Introduction

Worldwide, active research has been carried out over the last two decades in the synthesis of PSZ to meet the extensive demand of engineering ceramics [1]. The technologically interesting microstructure of zirconia materials consists of a cubic ZrO_2 solid solution matrix containing homogeneously nucleated precipitate of t-ZrO_2. On aging in the two phase field, the precipitates coarsen and above the critical size transforms martensitically to m-ZrO_2 during cooling to room temperature [2].

It is well known that the reactions in zirconia systems at a relatively low temperature are slow due to the slow diffusion. Precipitation, eutectoid decomposition and ordering processes proceed very slowly and the equilibrium is difficult to achieve. Metastability of zirconia was studied [3] through equilibrium phase relations in CaO–ZrO_2 system. The influence of strain on the extent of cubic solid solution field due to the coherent nature of precipitation seems to be relatively small.

The precipitate morphology in CaO-rich ZrO_2 was detected to be rhombic in projection and had rounded faces and corners. Coalescence of precipitates structure forms zigzag or sandwich like local alternation of variants [4]. The morphology of t-ZrO_2 precipitate was studied in the systems Mg-PSZ [5] and Ca-PSZ[6]. They differ from that of MgO and Y_2O_3 in their equiaxed rounded shape. The difference in morphology is related to the difference in kinetic energy of precipitation and coarsening. Zirconia prepared via chemical synthesis is characterized by uniform grain morphology and narrow particle size distribution [7,8]. Different methods of wet chemical preparation as citrate process [9], coprecipitation with ammonia [10], precipitation with urea [11], polymeric route using polyvinyl alcohol [12] and alkoxide synthesis [13] are developed to yield tailored powders consisting of ultrafine and spherical particles with narrow size distribution. On the other hand, agglomeration and relatively low homogeneity are the dominant points of weakness for these chemical techniques [14]. So that the field is opened to innovation of new chemical techniques, seeking sinterable powders precursors.

In the present paper, the polymerization reaction between urea and formaldehyde was utilized for preparation of Ca-PSZ zirconia. The gel prepared was characterized via IR and TG. The calcined powder was

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followed by XRD and SEM to evaluate the phase composition and microstructure.

2. Experimental work

Reagent grade urea (Pool 13H 15 Ltd, UK), commercial formaldehyde solution (37–40%) and pure ethylene glycol (Aldrich) were used for resin preparation. Inorganic salts used are zirconium chloride (Fluka) and calcium nitrate. Urea, formaldehyde and ethylene glycol were used in the proportions 1:2:2 mols, while the salt solution of $ZrCl_4$ was used in concentration 4 mol for one mol urea. The reaction between urea and formaldehyde starts at pH $\simeq$ 8–9 and then proceeds with reflux at 70°C for about 15 min which are the optimum conditions as described elsewhere [7]. The inorganic salt solutions were added simultaneously with ethylene glycol during the polymerization reaction. The reaction then proceeds in acidic media pH $\simeq$0.5. Water and other byproducts were then pumped out under vacuum conditions at the same reaction temperature to avoid resin dissociation.

The gel resulting was characterized using FTIR spectrophotometer (using potassium bromide method) and TG using Perkin–Elmer Thermal Analyzer at a rate of heating of 10°C/min. up to 600°C. The resin was poured in a petri dish (15 cm in diameter), dried and then calcined in an atmosphere of air following the results of TG up to 600°C. The developed crust was divided into pieces that were further heat treated at different temperatures. Some pieces of the crust were ground in the form of powders for XRD investigation. Other pieces of the crust were fired at 1300, 1400, 1500°C/2 h for SEM investigation. Phase analysis was carried out using Philips XRD Apparatus Type PH 9920/05 (Cu-target and Ni-filter). Crystallite size was calculated using sherrer formula $D = \frac{0.9\lambda}{\beta \cos\theta}$ (where D is the crystallite size, λ is the wavelength, β is the peak half width and θ is the diffraction angle). The percentage of monoclinic was calculated using the method described by Porter and Heuer [2]. Peaks used for calculation are $(\bar{1}11)^m$, $(111)^t$ and $(111)^c$. The microstructure was studied using SEM model Philips XL-30 attached with EDAX unit with accelerating voltage 30 kv.

3. Results and discussion

The polymerization reaction between urea and formaldehyde started in a neutral or slightly alkaline pH and was considered as a condensation reaction, thus urea reacting with formaldehyde eliminating water molecule. Reaction was terminated in acidic media at pH ~0.5. Zirconium chloride anhydrous and calcium nitrate solutions were added simultaneously with ethylene glycol, while polycondensation reaction proceeds. Crosslinked structure including Zr^{+4} linking in the polymer resin structure is made in an attempt to prepare fine ceramic oxide powder through polymer calcination. Transparent polymer resin without any signs of precipitation resulted in indicating high homogeneity. Salt solutions added simultaneously with the chosen alcohol (ethylene glycol) are acting as a catalyst in the polymerization reaction. The resin characteristic peaks on IR-pattern in Fig. 1 exist at 3400, 1637, 1400 and 1070 cm^{-1} representing NH_2-stretching (symmetric and asymmetric), NHC=O band characterizing polyamide resin, CN and NH stretching vibrations. The recorded shifts in these peaks indicate metal ions substitution in the resin. The metal Zr^{+4} linking was achieved completely through the use of a suitable reaction-terminating agent for the polymerization reaction, ethylene glycol. Chlorine anion does not participate in the polymer structure but volatilized as NH_4Cl during the calcination between 200 to 300°C similar to the conditions described by Djurcic et al. [15]. The valency of Zr^{+4} and its coordination number play a role in the degree of substitution in the resin structure. Thermogravimetric analysis in Fig. 2 displayed the dissociation reaction of organic matter in two steps. The first step ends at 200°C and the second step occurs between 200–600°C corresponding to total weight loss of about 50%. The maximum rate of gel degradation was calculated from the peak position to be at 190°C as shown in the DTG curve in Fig. 2. Polymer was calcined following TG and DTG results up to complete dissociation at 600°C.

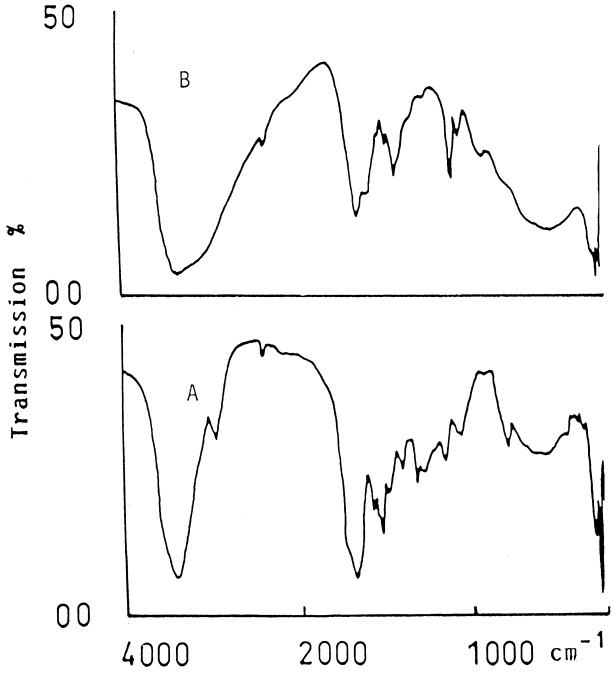

Fig. 1. IR patterns of the prepared resins; A. resin free of cations; B. resin hosting cations.

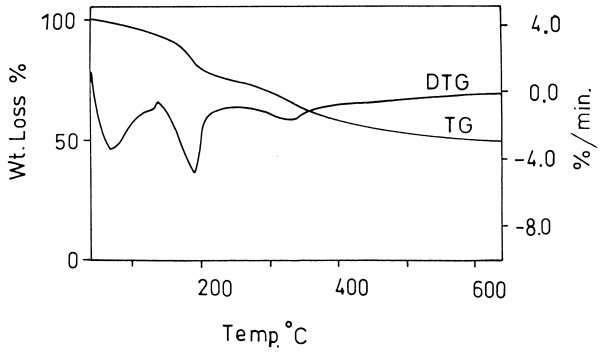

Fig. 2. TG and DTG of the resin hosting Zr^{+4} and Ca^{+2} cations.

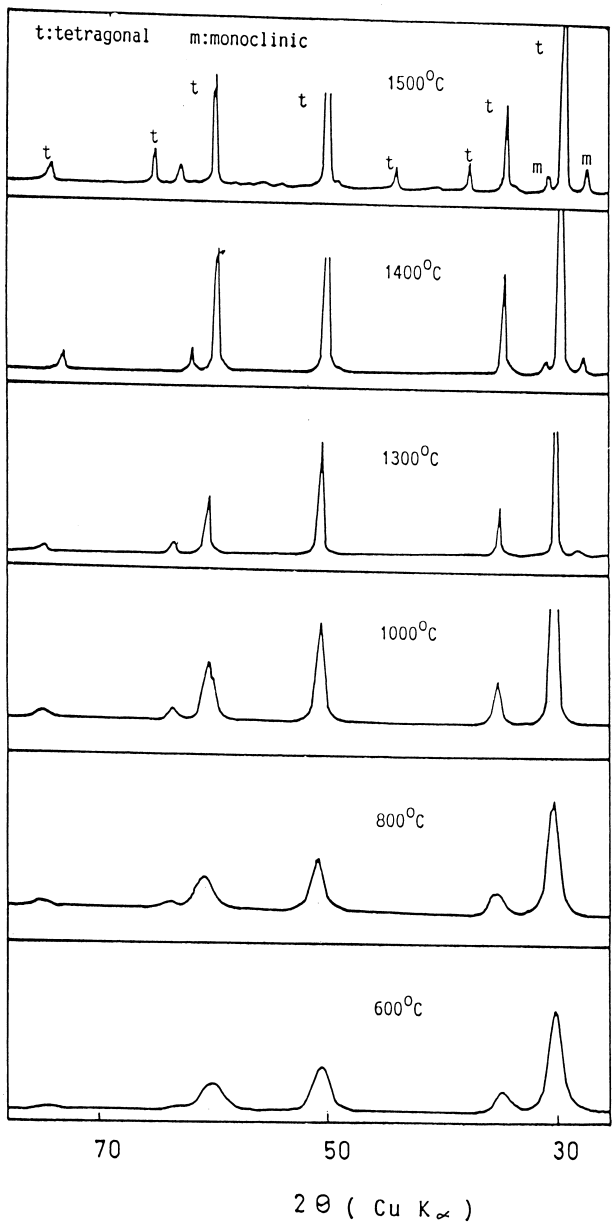

Fig. 3. XRD patterns of powders fired at different temperatures.

XRD patterns in Fig. 3 show a cubic solid solution that crystallized from amorphous materials at temperatures 600, 800, and 1000°C. Tetragonal zirconia was recorded at 1300°C/2 h with the least amount of monoclinic phase. Tetragonal zirconia was formed by precipitation from cubic zirconia solid solution through nucleation and crystallite growth. A small amount of grains reach the critical particle size and transform into m-ZrO_2, (Table 1). Nucleation of t-ZrO_2 proceeded simultaneously with crystallite growth at 1400°C/2 h. Tetragonality decreases with raising temperature up to 1500°C/2 h due to the increase of m-ZrO_2 at the expense of t-ZrO_2.

The influence of strain on the extent of cubic solid solution field due to the coherent nature of precipitation seems to be demonstrated in the present case. The critical particle size may be less than 21.8 nm as demonstrated in Table 1. Transformation proceeds by nucleation associated with grain growth to the critical size, where nucleation is autocatalytic (stress and strain assisted) as reported by Dickerson et al. [16]. The result is different from that reported by Kumar and Pramanik [12] where cubic zirconia remains non-transformed up to 1400°C, while transform to t-ZrO_2 in the present case.

Samples fired at 1500°C/2 h displayed a general view [Fig. 4(a)] with more or less equal size batches with interconnected pores different in size and shape. Cracks took place along the grain boundaries [Fig. 4(b)]. Further magnification to more than 7000, two clear generations of grains were clearly differentiated in specimens fired at 1400 and 1500°C/2 h. Major phase is a compacted grain more or less equigranular in size and cubic in shape. The second minor equiaxed rounded shape phase seems to be nucleated from the main phase and grown in size. These particles are set up first to t-ZrO_2 precipitate and formed by nucleation through eutectoid decomposition from cubic phase zirconia. Precipitate grains are separated and then accumulated in grain boundaries, [Fig. 4(c)] after reaching the critical size. EDAX of the small equigranular phase displayed in Fig. 5 showed that they are formed of ZrO_2 and CaO indicating that transformation is related to precipitate growth above the critical size. XRD analysis

Table 1
The crystallite size and the monoclinic percentage of 10 mol% CaO/ZrO_2 sample fired at different temperatures for 2 h

Temperature (°C)	Crystallite (Å)			Monolinic (%)
	Monoclinic	Tetragonal	Cubic	
600	–	–	53	–
800	–	–	55	–
1000	–	–	94	–
1300	219	218	–	6
1400	234	231	–	9
1500	260	239	–	13

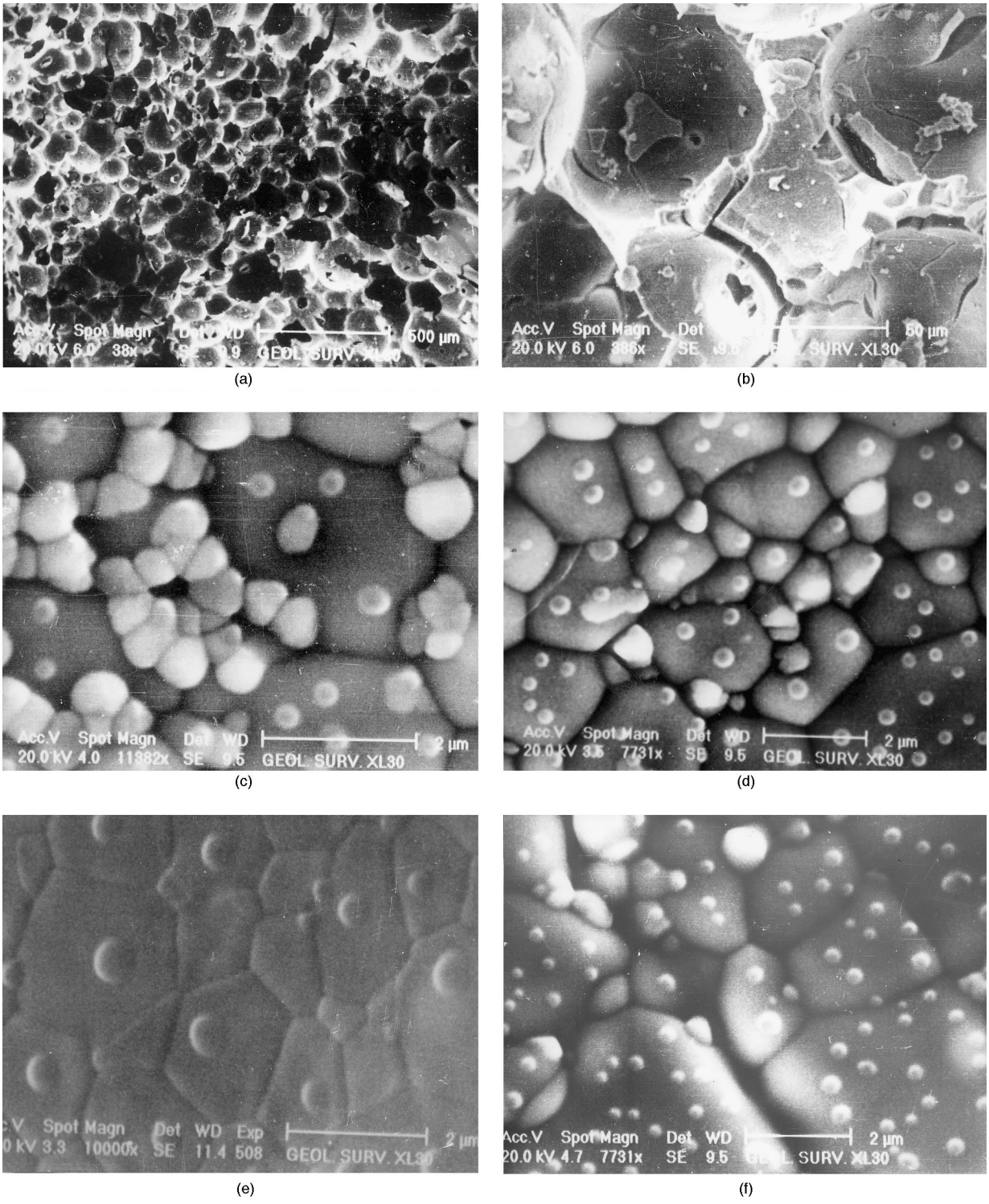

Fig. 4. SEM of as-recieved powders fired at different temperatures: (a)–(e) samples fired at 1500°C/2 h; (f) sample fired at 1400°C/2h.

in Fig. 3 displayed two main phases, t-ZrO_2 with a minor amount of m-ZrO_2 reaches 13% at 1500°C/2 h. The result is related to eutectoid decomposition studied by Porter and Heuer [2]. The best materials are those in which precipitation reaction of t-ZrO_2 in cubic matrix is about two thirds complete and the precipitate did not lose coherency. Under these conditions, particles do not transform to m-symmetry when cooled to room temperature except near propagating cracks. When the two thirds precipitation reaction is complete, overaging commences and twinning exists. The material then lost most of its propensity for toughening, since twinning

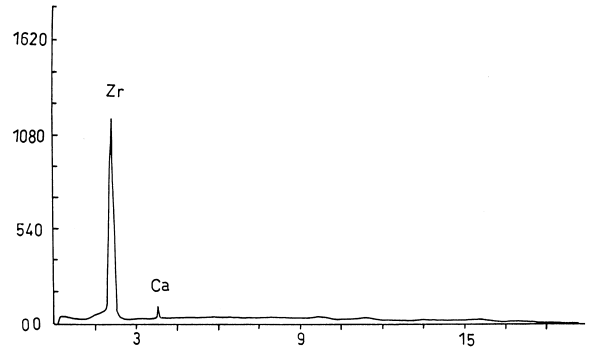

Fig. 5. EDAX of small equiaxed grains nucleated and grown from t-ZrO_2 precipitate in sample fired at 1500°C/2 h, [Fig. 4(D)].

accommodates much of the transformation strain. The transition state between toughness control and steady state of cracking is of major significance, because it represents the optimum microstructure for enhanced toughness as printed by Evans [17]. Tetragonal ZrO_2 is nucleated from cubic solid solution and increase in size gradually with aging time and temperature rise. The present case displayed the precipitation reaction followed by transformation of t-ZrO_2 precipitates into m-symmetry accompanied by grains separation and accumulation at the grain boundaries at 1500°C, [Fig. 4(d) and (e)]. At 1400°C, the precipitation reaction may exceed the two thirds without losing coherency where the precipitate seems to be equiaxed rounded grains as confirmed by SEM results. The decomposition of solid solution is related to temperature rise and strain factor. There are no fractures through grains but through grain boundaries, indicating higher toughness and strength of grains [Fig. 4(e)]. The strain energy associated with the precipitation reaction is clearly important. In a model of a strain energy calculation reported by Lanteri et al. [6], the morphology of t-ZrO_2 precipitates in Ca-PSZ, Mg-PSZ and Y-PSZ was assessed. The habit of t-ZrO_2 precipitate in Ca-PSZ is described to be equiaxed. The model is based on the initial formation of small coherent precipitates with arbitrary shapes and arbitrary distribution in a homogenous matrix. The difference in kinetic energy of precipitation and coarsening is the cause responsible for morphology changes with the stabilizer change as reported by Lanteri et al. [6]. The sample fired at 1400°C in Fig. 4(f) displayed the main phase grains with 1–2 μm in size. There is no chance for pore existence. At lower temperature 1300°C, the kinetics are slow enough and locally regular arrangements of precipitate are formed, such that two dimensional distribution of t-ZrO_2 precipitates exists. The precipitate formed in specimens fired at 1400°C/2 h are still coherent equiaxed grains as seen in Fig. 4(f). The coherent equiaxed rounded form of precipitate is related to primary type associated with growth under the critical particle size as described by Hughan and Hannink [5] in his study of Mg-PSZ under controlled cooling.

4. Conclusion

Microstructural control is a critical issue facing fabrications of advanced ceramics especially in polyphase ceramics. Tetragonal precipitate in this study was developed to a condition of metastability. The precipitate was transformed in the presence of stress-stain developed through nucleation and growth partially to monoclinic, when the particle size became above the critical grain size. The volume of critically metastable t-precipitate was maximized to more than 90% with controlled transformation. Controlling the average grain size and size distribution of the major phase is related to achieving the precipitation conditions. Tetragonal ZrO_2 precipitate prevents the abnormal grain growth and swallows pores. Combined with submicron size, narrow particle size distribution and homogenous materials, packing without any signs of pores exists without using forming applied stress. The resulting morphology is controlled through chemical preparation via polymerization reaction of urea with formaldehyde forming polyamide resin. Metal cations are distributed homogeneously within the structure of the resin.

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