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Effect of Oxide Additives and Particle Size on Stabilization of Treated Commercial Zirconia

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Commercial zirconia was milled and sedimented to separate finer and coarser particles. Then additives such as CaO and Y_2O_3 were added in proportions of 7 and 13 mol.% each. Wet mixing of these powders was done in the ball mill. These mixtures were then compacted through uniaxial compaction using 150 MPa of pressure to make pellets of 8 mm diameter and 3 mm height approximately. The compacts were sintered at 1700 °C under argon atmosphere during 1 h. Densification calculations revealed densities of more than 80% in all samples. Scanning electron microscopy (SEM) showed that closed porosity was present. X-ray diffraction (XRD) results confirmed the presence of cubic phase with quantities higher in samples of finer powder and 13 mol.% additive.

Keywords oxide additives, sintering, stabilization, zirconia

Introduction

Stabilized and partially stabilized zirconia powder has been the subject of interest and an active field of research since 1975, when Garvie *et al.*[1] published the first significant work concerning the toughening of zirconia through stabilization. Some time later, it was followed by the papers of Porter *et al.*[2–4] on the same subject. Heuer[5] published a detailed work in 1987 in which he discussed at length the transformation toughening of ceramics containing zirconia. He not only discussed the structural changes but also gave a detailed view of the mechanical properties, especially the *R*-curve behavior of such materials. This is the phenomenon that retards the growth of cracks in transformation toughened ceramics, thus increasing their toughness. Since then, owing to the improvement in properties and the consequent usefulness in different engineering applications, toughened zirconia and other ceramics containing it have become a very useful tool in the hands of a material scientist and engineer.

Toughening of zirconia takes place through spontaneous martensitic transformation when cooling from the tetragonal to monoclinic phase under precise and controlled conditions. The same transformation, which results in an ~5 vol.% increase on cooling, if not properly controlled, may result in degradation and destruction of the sintered component. Many techniques are used to stabilize or partially stabilize the tetragonal phase of zirconia at working temperatures. A large amount of work has been done to study the effect of particle size, and additives, so that a partially stabilized, metastable tetragonal phase can be obtained at room temperature.[6–9] Addition of the appropriate amount of metal oxides can assist in stabilization of tetragonal and cubic phases at lower temperature ranges and even at room temperature.[10] These additives of lower-valent cations provide oxygen vacancies that help in compensating defects, and the cations being of smaller radii help in relaxing the matrix, thus avoiding the cracking during t-ZrO_2 to m-ZrO_2 transformation during cooling. The sol-gel process is employed for the production of nanometric pure as well as stabilized and partially stabilized zirconia.[11] Chemical methods such as chemical vapor deposition (CVD) and hydrothermal oxidation are used, which have been studied by Somiya and other authors.[12–14]

X-ray diffraction (XRD) is one of the most common techniques for conducting the phase analysis of zirconia. The diffraction patterns of zirconia in 2θ ranges from 27 to 32° and 72° to 76° reveal the $m/(c,t)$ and c/t intensity ratios, respectively.[15] The peak of t-ZrO_2 is not easily distinguished from c-ZrO_2 at these angles.[15–17] In the ZrO_2-Y_2O_3 system, a specific tetragonal phase t'-ZrO_2 has been observed in addition to the equilibrium polymorphs.[18] This phase is formed during sintering in the stability range of the cubic phase of the system equilibrium diagram, provided the succeeding cooling rate is rapid enough. Though different from equilibrium t-ZrO_2, this phase is hard to resolve from the equilibrium tetragonal by XRD, because only a slight angular difference between (004) and (400) at high angles has been observed. Transmission electron microscopy allows distinguishing between the two phases. Many novel techniques have been adopted for production of doped and pure zirconia powder. Hydrothermal synthesis is popular for synthesis of doped ZrO_2.[19]

The powder particle size plays a very important role in the sintering and stabilization of zirconia. Much work is being done on nanosized zirconia powder. Duran and co-workers[20,21] have done important research on this topic. They have published their work based on Y_2O_3 added zirconia powder, which was prepared by the chemical coprecipitation method. The authors tried to obtain theoretically dense and defect-free ceramics by the pressureless sintering of this powder. They concluded that nanosized zirconia powder could be used to produce fully dense ceramics by sintering at low temperatures but for a longer period of time. The nanocrystalline partially stabilized zirconia

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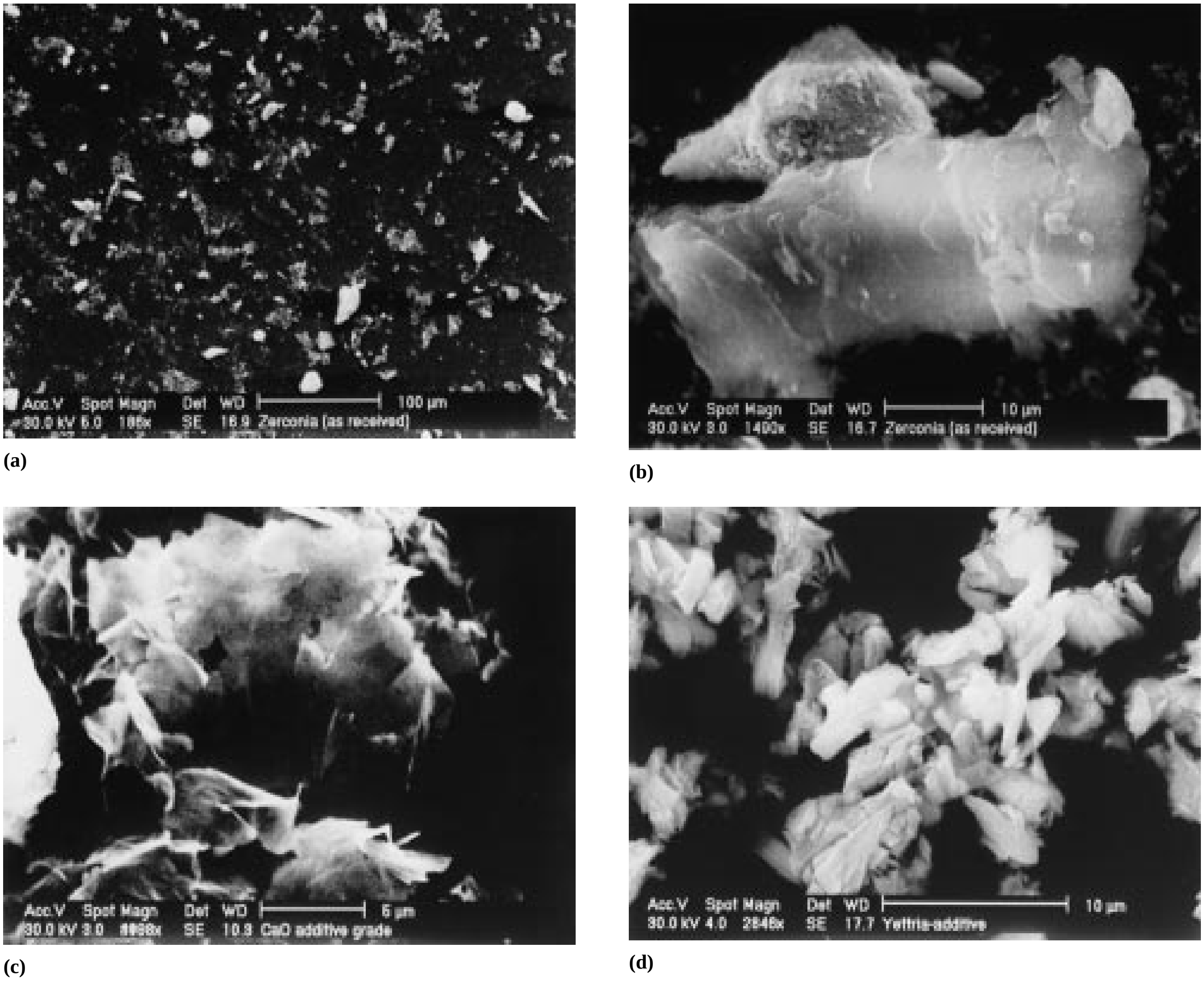


Fig. 1 SEM micrographs of (**a**) and (**b**) untreated ZrO_2, (**c**) CaO additive, and (**d**) Y_2O_3 additive

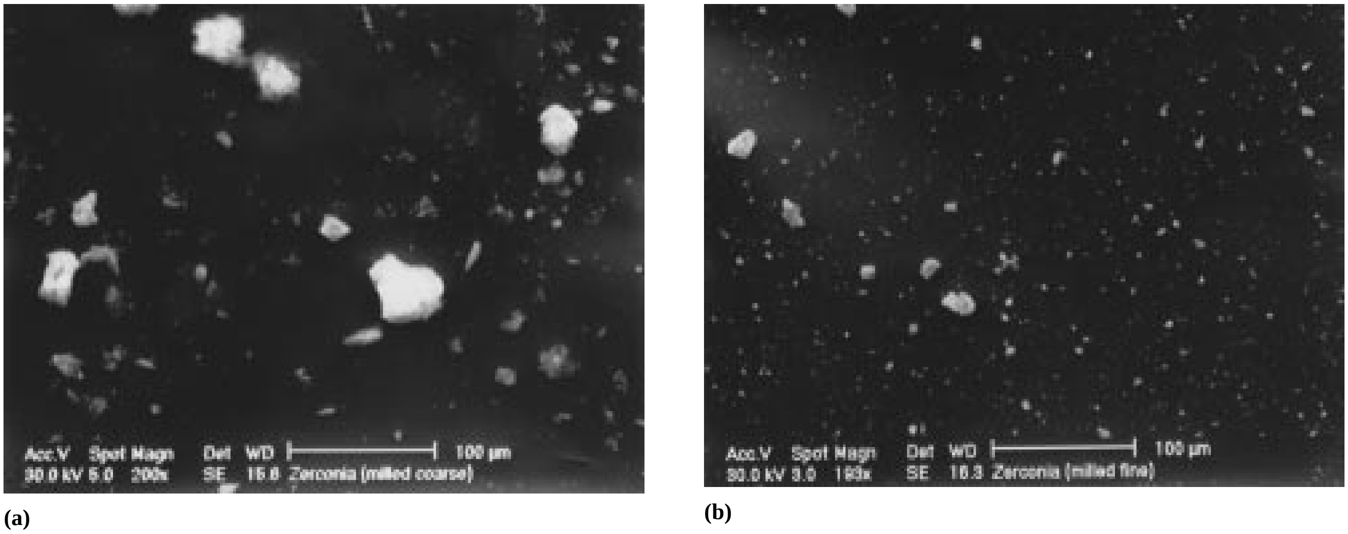


Fig. 2 (**a**) Coarse powder separated by sedimentation. (**b**) Fine zirconia powder

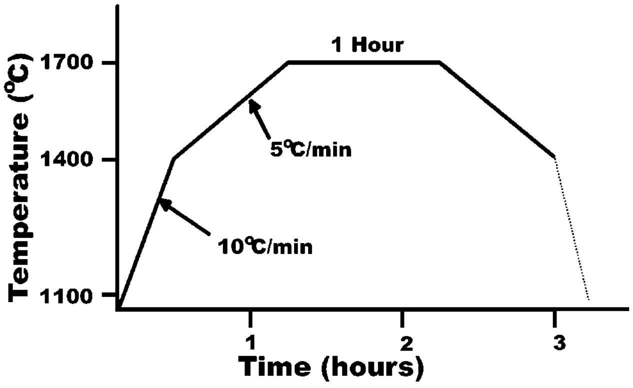


Fig. 3 The sintering cycle used for experiments

Table 1 Compositions of samples. Each row shows the details of one sample

Wt. of ZrO_2 (g)	Powder Type	Wt. of additive (g)	Mol.% additive	Additive
5	*C*	0.63	7	Y_2O_3
5	*C*	1.17	13	Y_2O_3
1.5	*F*	0.189	7	Y_2O_3
1.5	*F*	0.351	13	Y_2O_3
5	*C*	0.14	7	CaO
5	*C*	0.26	13	CaO
1.5	*F*	0.042	7	CaO
1.25	*F*	0.065	13	CaO
6.67	*C*	0.14	7	MgO
6.67	*C*	0.26	13	MgO

Table 2 Tabulation of densification results of the samples

Sample	Composition	Theoretical density (g/cm^3)	Apparent density (g/cm^3)	Percentage densification
1	(*C*) ZrO_2 + 7 mol.% Y_2O_3	5.4408	4.36	80%
2	(*C*) ZrO_2 + 13 mol.% Y_2O_3	5.3825	4.27	79%
3	(*F*) ZrO_2 + 7 mol.% Y_2O_3	5.4408	4.73	87%
4	(*F*) ZrO_2 + 13 mol.% Y_2O_3	5.3825	4.32	80%

with yttria additives (Y-PSZ) has been produced using zirconium alkoxide and yttrium acetyl acetonate as the ceramic precursors. They were characterized using the Rietvelds method, and it was concluded by the authors of this work[22] that the averaged crystallite size and lattice mismatch calculated in this way are in good agreement with those calculated by other methods. In addition to this, nanosized zirconia has also been prepared by a new sol-gel process, which involves the addition of excess C_2H_4O into aqueous $ZrOCl_2$ solution and carrying out the reaction at room temperature.[23] Bandyopadhyay[24] and colleagues have proposed a novel technique for the synthesis of fine zirconia, which uses a simple electrochemical method for the synthesis.

Our work deals with the study of oxide additives on treated commercial zirconia powder. The effect of the sintering atmosphere and different sintering cycles has also been studied. The correlation between particle size and entrapped *t*-ZrO_2 in the sintered samples has been studied XRD.

Experimental Work

The initial ZrO_2 powder was a commercial grade powder present in pure monoclinic form. This fact was established through XRD (Philips PW 3710, Philips Electronic Instruments Corp., Mahwah, NJ). The XRD plot is shown in Plot 1. The scanning electron microscopy (SEM) was performed on a Philips XL30, supplied with an energy dispersive spectroscopy (EDS) probe. The morphology and structure of the powder particles are shown in the Fig. 1(a). Figure 1(b) shows that there exists a wide range of particle sizes in the powder. We believe that an explanation can be given for such an observation. Probably, larger particles were present in tetragonal form, but, at the end of the manufacturing process, due to rapid cooling, they transformed into very small monoclinic phase particles in the presence of stress due to cooling. In Fig. 1(c), a micrograph of CaO shows that the powder has a low quality. Its particles have a large distribution of sizes and shapes. They are mostly present in agglomerates. The Y_2O_3 powder is shown in Fig. 1(d). It is a good quality powder with finer particles, less agglomerates, and a relatively narrow size range.

The initial ZrO_2 powder was milled in a ball mill (RETSCH PM400) to reduce the particle size, at 75 rpm for 1 h using an alumina jar and alumina balls. This process reduced the size of the powder and broke the hard agglomerates, if any. After this, sedimentation of the powder was done in an aqueous solution using a graduated cylinder with NH_4Cl as a dispersant. The sedimentation process was used to separate the powder into two types, coarse and fine zirconia powder, on the basis of their particle size distribution.

The SEM micrographs in Fig. 2(a) and (b) show the two powders separated by sedimentation. Comparing these micrographs with each other, we can see the success of the separation. From now on, the powder in Fig. 2(a) will be referred to by the symbol *C* for coarse particles, and the powder in Fig. 2(b) by the symbol *F* for fine particles.

Different samples were prepared by adding the two additives in each category of powder, the details of which are given in Table 1. The table shows that 7 and 13 mol.% of each additive were used. These proportions were selected because this allowed us to compare the effect of different additive concentrations. Wet mixing in ethanol was used to mix these powders in a ball mill at 75 rpm for 20 min under similar conditions as described previously. They were then taken out, dried, and again milled for

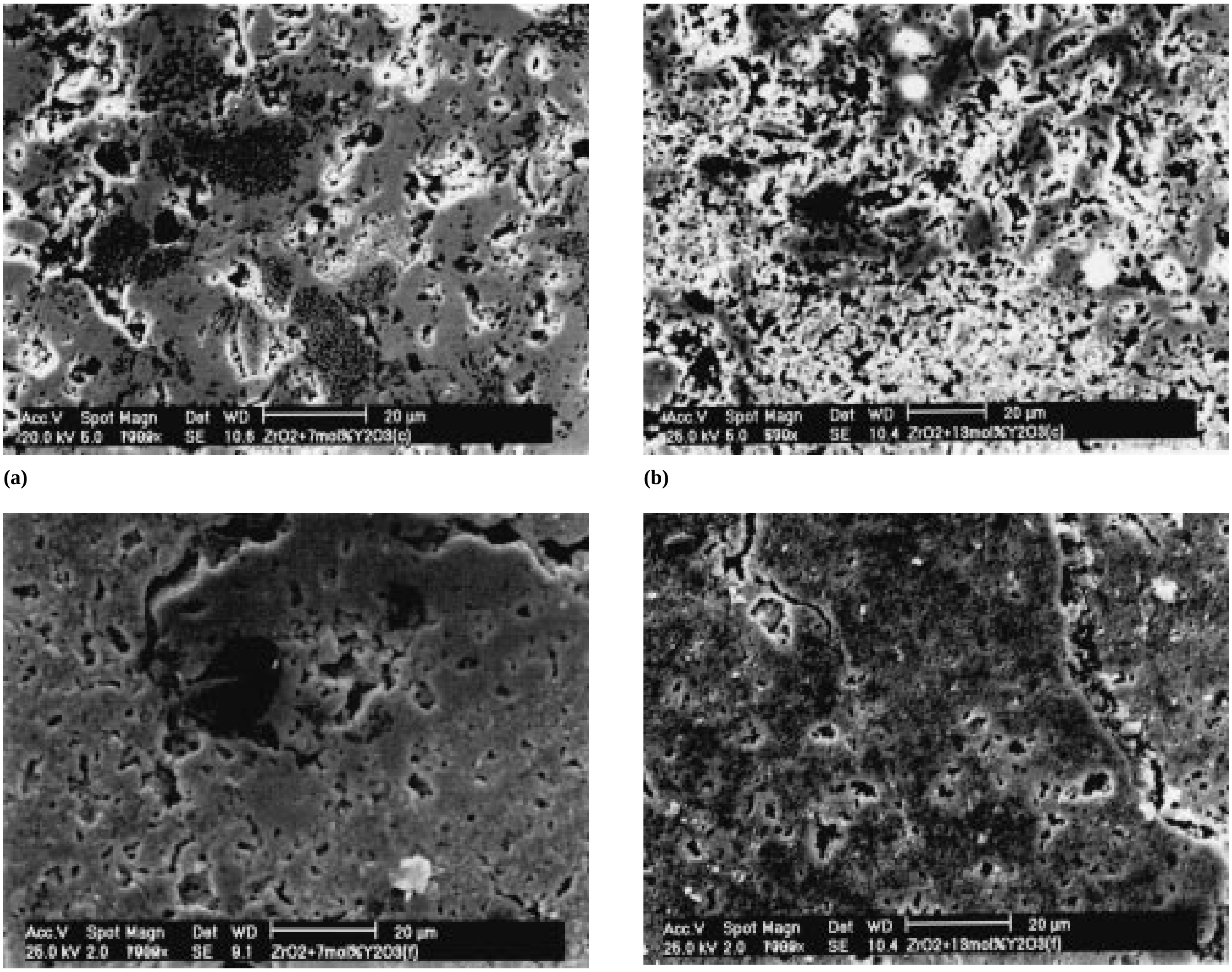


Fig. 4 Micrographs of (**a**) sample 1: $ZrO_2(C)$ with 7 mol.% Y_2O_3; (**b**) sample 2: $ZrO_2(C)$ with 13 mol.% Y_2O_3; (**c**) sample 3: $ZrO_2(F)$ with 7 mol.% Y_2O_3; and (**d**) sample 4: $ZrO_2(F)$ with 13 mol.% Y_2O_3

10 min at 75 rpm. After mixing, the powders were compacted through a uniaxial, hydraulic compression machine. A pressure of 150 MPa was used on a die of 8 mm diameter.

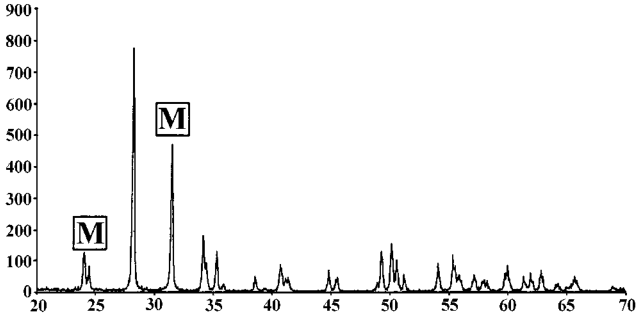
Compaction was followed by sintering in a high-temperature furnace under argon atmosphere at 1700 °C. The sintering cycle is presented in Fig. 3.

Study of Sintered Samples

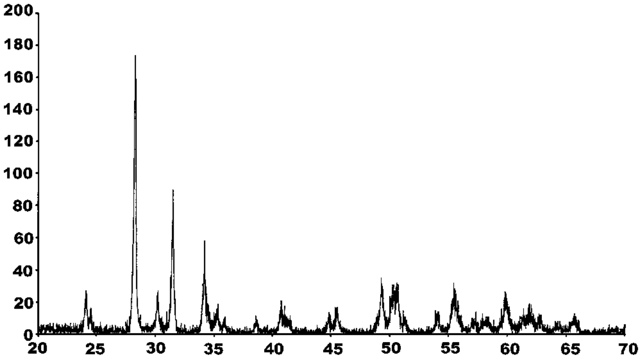
Densification of the sintered samples was calculated by measuring the dimensions after polishing and comparing them to the theoretical density of the mixture. The results for densification obtained for samples only containing yttria as the stabilizing agent are given in Table 2. The table shows that samples of powder *F* have greater density than the other two. A lower densification of sample 4 can be explained by the presence of a crack inside the sample.

These samples were then studied for more detail by SEM and XRD. Results for SEM are given in Fig. 4. By comparing the micrographs of the four samples, we see that the samples of powder *C* have less density and are more porous than the *F* powder samples. The reason for this is that the particles of powder *F* are much finer than those of the other powder. Also, in Fig. 4(d), a crack can be observed on the surface of the sample; this could possibly be one reason it shows a low apparent density.

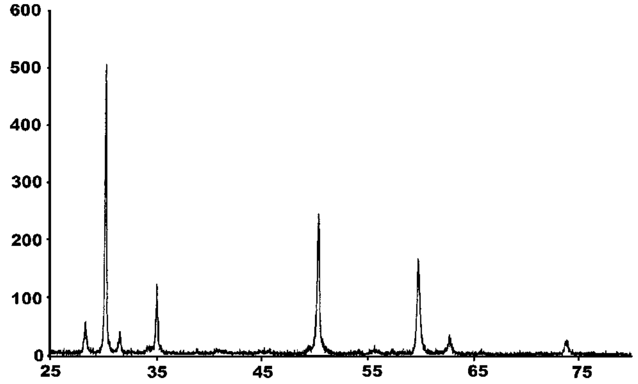
Plot 1 gives an XRD pattern of pure as-received zirconia powder. Plots 2 to 6 are the XRD patterns of the sintered samples. When compared to Plot 1, we see that the peaks representing the monoclinic phase gradually come down in intensity and finally disappear in the sintered zirconia $(F) + 13$ mol.% Y_2O_3. The peaks for the cubic phase increase their intensity in the same respect. We see that Plot 2 of the sample with CaO as the additive has a lot of noise in it. An emergence of the cubic peak can be seen but is almost negligible. The graphs of the samples with Y_2O_3 as the additive show much better results with prominent



Plot 1 XRD plot of the initial zirconia powder. The peaks highlighted by M are the two representative peaks of the monoclinic phase



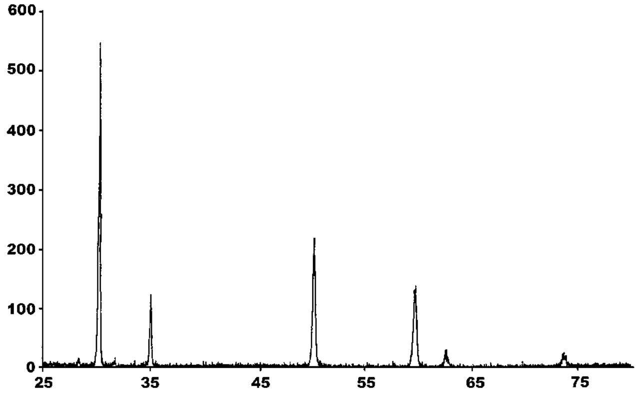
Plot 2 Graph of sample with $ZrO_2(C)$ and 7 mol.% CaO



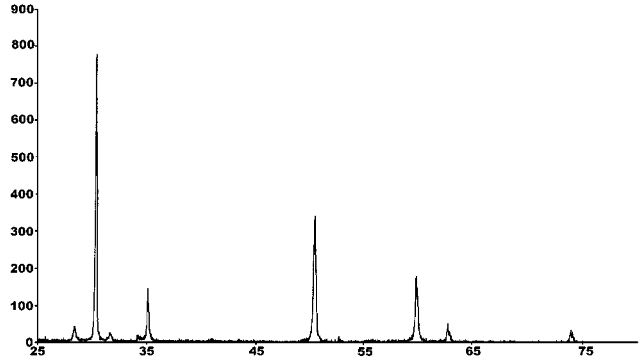
Plot 3 XRD plot of sample 1: $ZrO_2(C)$ + 7 mol.% Y_2O_3

peaks of cubic phase. These peaks increase in intensity as the mol.% of the additive increases. The reverse happens to peaks signifying monoclinic phase.

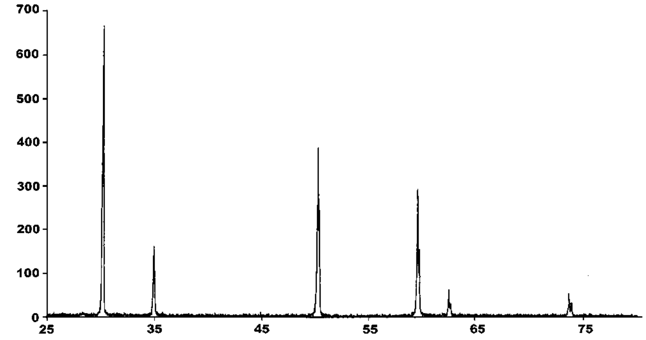
The XRD results show that CaO and MgO have a very insignificant effect on the monoclinic phase. Only one representative XRD pattern is shown in Plot 2, where peaks of unreacted/undissolved CaO are also present. This signifies incomplete sintering. The sintered density in the case of samples with CaO and MgO was always below 80%. Table 2 only gives density values for samples with the yttria addition, as these were the only samples with significant cubic phase and appropriate sintered density.



Plot 4 XRD plot of sample 2: $ZrO_2(C)$ + 13 mol.% Y_2O_3



Plot 5 XRD plot of sample 3: $ZrO_2(F)$ + 7 mol.% Y_2O_3



Plot 6 XRD plot of sample 4: $ZrO_2(F)$ + 13 mol.% Y_2O_3

Conclusions

The objective of this study was to establish the importance of particle size and morphology (zirconia and additives) on the stabilization of sintered components. The starting powder was a mixture of treated and separated zirconia with different quantities of additives. The samples produced using fine zirconia exhibit a higher density and an absence of monoclinic phase. The following can generally be concluded.

- The quality of additives is directly related to the sintering and stabilization of zirconia. Calcium oxide and magnesium oxide performed poorly as an additive because of nonuniform particle shape and size and also due to the presence of a large number of agglomerates. The density measurements and XRD results support Y_2O_3 as the most suitable additive, partly because of its nature and partly because of its morphology and size.

- The type of zirconia powder plays a very important role. The coarser the powder, the more unsuccessful the sintering and stabilization. These results can be drawn by studying the densification, SEM micrographs, and XRD plots of the four samples containing yittria presented in Table 2.

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