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Sintering behaviour of mechanically alloyed and coprecipitated 12Ce–PSZ powders

S. MASCHIO, A. BACHIORRINI
Dip. di Scienze e Tecnologie Chimiche, Via Cotonificio 108,-33100 Udine, Italy
E-mail: stef.maschio@dstc.univd.it

E. LUCCHINI
Dip. di Ing. dei Materiali e Chimica Applicata, via A. Valerio 2, 34127 Trieste, Italy

A comparsion was made of the sintering behaviour of 12Ce–PSZ powders prepared by coprecipitation and by mechanical alloying. Despite the presence of large aggregates, samples prepared from the chemically produced powders reached a high density after 3 h sintering at 1450 °C. The samples obtained by mechanical alloying of powders had the highest green density. However, owing to their wide agglomerate distribution and low-temperature agglomeration rate, they do not reach high density even after prolonged soaking at 1450 °C. The mechanically alloyed powders were flo-deflocculated to remove agglomerates as well as the electrostatic charge formed during their preparation. This treatment improved pressureless sinterability in air, and final densities close to the theoretical value were obtained. © *1998 Kluwer Academic Publishers*

1. Introduction

The production of ceramic oxide materials with a fine grain size has stimulated research into sophisticated synthesis routes for powder preparation in order to obtain nanometre-sized particles [1–4].

Particle dimensions and shape have a strong influence on powder activity and on the possibility of forming high-density green compacts. The smaller the particle dimension, the lower is the sintering temperature and/or the shorter the sintering time. If a solid solution is desired, chemical methods (i.e. coprecipitation and sol–gel) yield a fine dispersion of the amorphous components, which can be crystallized at a lower temperature with respect to traditional ceramic processes. Such routes are also useful when a mechanical mixture of two phases with similar crystallization temperatures is required [5–9].

Particle size, shape and distribution are all very important parameters in the densification of ceramic materials. Nanometre-sized particles produce very small grains and pores but, in many cases, such powders contain agglomerates which retard the sintering process.

Mechanical alloying has been recently presented as a new method for realizing nanocrystalline particles. However, this process is relatively new and its application to oxide ceramics has not yet been satisfactorily studied.

Dry milling of metals and ceramics has been investigated by several researchers [10–14], who have demonstrated that with this procedure it is possible to obtain solid-state reactions between components to form new crystalline phases and/or reduce the crystallite size of starting powders. Treatment at room temperature to obtain ceramic oxide solid solutions is a promising method of synthesizing materials with fine microstructures. Unfortunately, milled ceramic oxide powders do not reach high density values in pressureless sintering processes [15, 16] and very few works have examined the sintering trend of such products in pressureless experiments. More research and new treatments would therefore seem to be necessary to improve powder sinterability.

In this study, 12Ce–PSZ powders were prepared for sintering by coprecipitation and mechanical alloying, and their behaviour subsequently compared, as these powders are a concrete example of an oxide ceramic solid solution that reaches high density and has good mechanical properties [17–26]. Powders produced by mechanical alloying were further treated by a physical-chemical method [27, 28] to reduce their wide agglomerate distribution and improve sinterability.

2. Experimental procedure

Cerium nitrate hydrate (Aldrich Chemicals 99%) and zirconium oxychloride hydrate (Aldrich Chemicals 98%) were dissolved in distilled water and coprecipitated in diluted ammonia (two parts by volume of water to one part of ammonia) and then treated as described elsewhere [16] to produce 12Ce–PSZ. The powders were calcined for 1 h at 600 °C, quenched in air and wet milled (2 h) in a plastic jar with zirconia balls in isopropylalcohol.

Monoclinic zirconia (TZ0-Tosoh) and cubic ceria (99.9% Janssen Chimica, 2340 Bearse, Belgium) weighted in appropriate proportions were used as starting oxides in the mechanical alloying route. A total of 1 g powder and six Y-TZP spheres (9 mm diameter, Tosoh) in a Y-TZT jar (Spex product) were used for each milling process. After 12 h milling in a Spex 8000, only the tetragonal solid solution was detected. Shorter milling times produced a mixture of both the tetragonal and monoclinic phases.

In this procedure, after 12 h milling, a contamination of the starting powders in Y–TZP of 5% by weight was measured, which corresponds to a contamination in yttria of about 0.1% M. We considered this level to be insignificant and insufficient to affect powder properties.

The final product was divided into two batches. The first was used as-prepared and the second was flo-deflocculated [27, 28] using diluted HCl as the acid environment promoter and NH_4OH as the flocculating agent for a suspension containing 5 vol % powder in distilled water.

X-ray diffractions were performed with an Inel instrument using cobalt radiation and crystallites dimensions were evaluated by a JEM 2000EX transmission electron microscope. Specific surface areas (BET) were measured using a Sorptomatic 1900 Carlo Erba and agglomerate size distribution was evaluated with a Coulter LS 130 instrument. Cylindrical samples were obtained by uniaxial pressing at 50 MPa followed by isostatic pressing at 200 MPa. Green body densities were determined from the ratio between weight and volume; sintered densities were evaluated by the water displacement method. Shrinkage of the green samples was monitored by an alumina dilatometer up to a temperature of 1500 °C at a heating rate of 10 °C min^{-1}. Further sintering tests were performed in air in a Netzsch muffle equipped with $MoSi_2$ heating elements. Microstructures were examined using a Cambridge Stereoscan 430 scanning electron microscope and average grain size was evaluated by the lineal intercept technique.

3. Results and discussion

Separate milling (12 h) of pure monoclinic zirconia leads to a pure tetragonal phase but even prolonged milling of ceria does not modify its cubic structure although the reduction of crystal size determines a broadening of the diffraction peaks.

Unalloyed cubic ceria in the milled mixture should be revealed by the presence of a shoulder in the (1 1 1) tetragonal reflection peak but this was not detected after 12 h milling. Fig. 1 shows the X-ray diffraction patterns of the pure oxides (a, b), and their mixture after (c) 6 and (d) 12 h milling. We can therefore assume that in all the powders submitted to the sintering tests, ceria is completely dissolved into the tetragonal zirconia cell.

Table I gives the characteristics of the starting powders and the density of the green samples. It is possible to note that coprecipitated powders have specific surface area higher than mechanically alloyed (46 versus, 12 $m^2\,g^{-1}$) and flo-deflocculation further reduces this latter value. Crystallite size is also a function of powder preparation, being 30 nm for coprecipitated and 10 nm for both the mechanically alloyed powders. It may be also pointed out that the green density is strictly dependent on powder preparation procedure, because samples formed with mechanically alloyed powders (i.e. MA° and MA′) have the highest values. In Fig. 2, the Coulter spectra of particle distribution show that most of the agglomerates of coprecipitated powders (curve CP) were in the range 5–50 μm with a high concentration of particles around 20 μm. A significant proportion (10 vol %) had larger dimensions (> 150 μm). Mechanically alloyed powders had most of the particles in the range between 2 and 200 μm (curve MA°) but agglomerates with greater dimensions disappeared in the flo-deflocculated (curve MA′).

Fig. 3 shows scanning electron micrography of the (a) coprecipitated, (b) mechanically alloyed, and (c) flo-deflocculated powders. In (a), a mixture of small particles, agglomerates and large, irregular aggregates is visible. In (b), very small particles and more regular agglomerates can be observed (aggregates were not revealed). Fig 3c has a greater magnification than (a) and (b), and shows a closer view of the agglomerates.

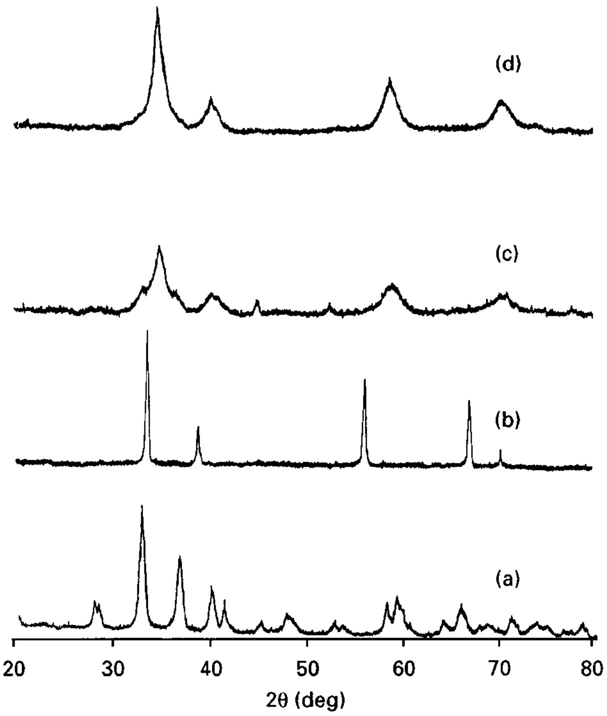

Figure 1 X-ray diffraction patterns of monoclinic zirconia (a) ceria, (b) a stoichiometric mixture of the components milled (c) 6 and (d) 12 h.

TABLE I Specific surface area, average crystallite size, sample green density and relative density of starting products

Material[a]	Specific surface area ($m^2\,g^{-1}$)	Crystallite size (nm)	Density ($g\,cm^{-3}$)	Relative density (%)
CP	46	30	2.35	38
MA°	12	10	3.40	55
MA′	6	10	3.42	55.3

[a] CP = coprecipitated, MA° = as-milled mechanically alloyed, and MA′ = flo-deflocculated mechanically alloyed powders.

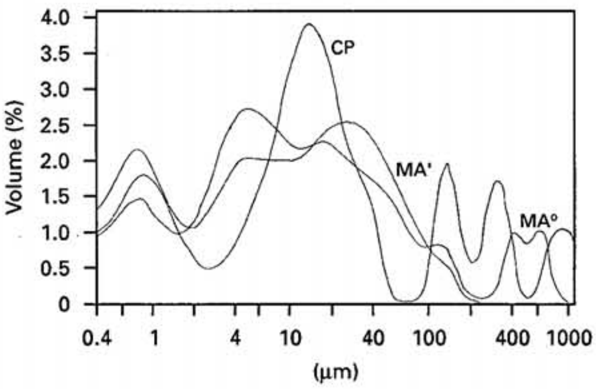

Figure 2 Coulter spectra of powders: CP = coprecipitated, MA° = mechanically alloyed, MA′ = mechanically alloyed and flo-deflocculated.

In fact they look less open than in Fig. 3c and of slightly smaller dimensions. In this powder the quantity of small particles seem to be reduced, increasing the amount of medium size agglomerates. Photos are not representative for particle and/or agglomerate dimensions, but only for their shape and consistency.

Fig. 4 reports the dilatometric tests of the green samples. The sample prepared with chemically derived powders (CP) started to shrink at a temperature below 1000 °C and, although it might be possible to suggest that the process is in part due to volatile substances still entrapped in the powders, shrinkage proceeds at a high rate up to 1250 °C and then slows. In contrast, both the mechanically alloyed powders started to densify at higher temperatures (1240 °C) but MA° contracted at a moderate temperature (< 300 °C) whereas MA′ did not. Both powders had tetragonal symmetry before and after this moderate temperature (as was confirmed by X-ray diffraction of the samples), so the contraction is probably due to a change in powder morphology.

The slope of the three curves diminished at 1410 °C (MA°), 1320 °C (MA′) and 1270 °C (CP), respectively. We believe that these temperatures correspond to the end of the first step of the sintering process [29, 30] and to the start of grain growth. For both the mechanically alloyed products, this begins at higher temperatures than for the coprecipitated products. It follows that if we sinter all the samples at 1450 °C, grains of CP specimens can grow for a longer time. This is confirmed in Fig. 5a–c, which shows the microstructures of the samples fired for 3 h at 1450 °C. Materials produced with CP powders have coarser microstructures (1.5 μm) than those produced by mechanical alloying. Moreover, grains of MA′ samples are slightly larger (0.8 μm) than MA° (0.5 μm).

Fig. 6 reports density versus sample sintering time at 1450 °C. All samples reach the maximum value after 3 h of firing, but the density of CP specimens decreases for a longer soaking time due to the rise of the monoclinic phase. MA° and MA′ specimens do not suffer for this event as their grain size is much smaller. On the other hand, MA′ samples reach high density, while MA° do not.

MA powders are made of nanosized crystallites, but it is not possible to assume that all particles have nanometric size because, with our investigation instruments, it was not possible to evaluate particle-size distribution but only the distribution of particles, agglomerates or aggregates.

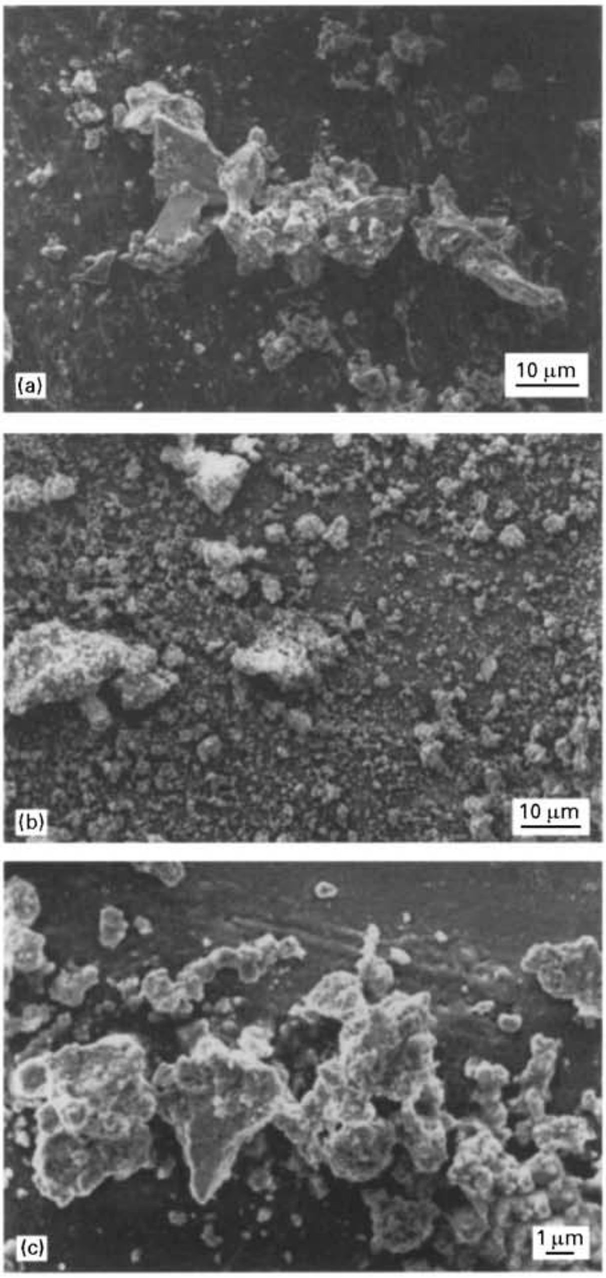

Figure 3 Scanning electron micrographs of powders (a) coprecipitated, (b) mechanically alloyed, and (c) mechanically alloyed and flo-deflocculated.

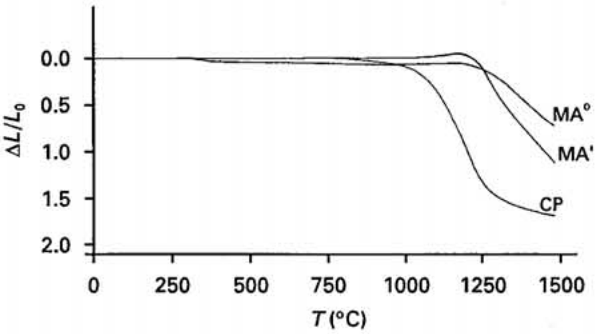

Figure 4 Dilatometric behaviour of the green samples: CP = coprecipitated, MA° = mechanically alloyed, MA′ = mechanically alloyed and flo-deflocculated.

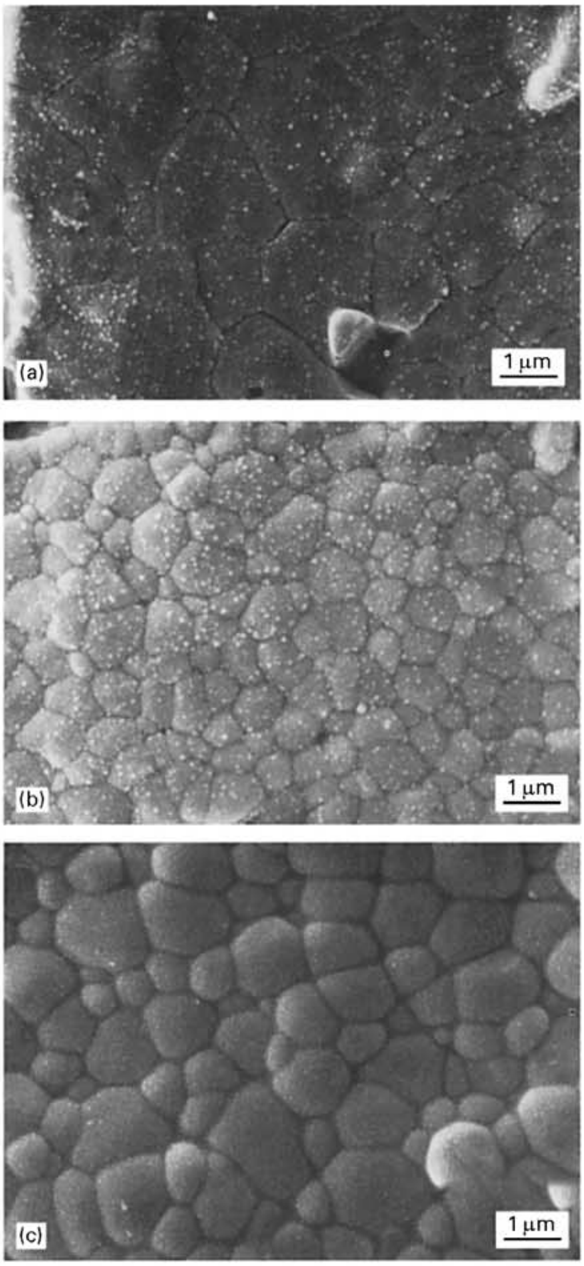

Figure 5 SEM microstructures after 3 h at 1450 °C: (a) coprecipitated, (b) mechanically alloyed and (c) mechanically alloyed and flo-deflocculated; bright particles are gold coating.

In a recent work [16], we performed a number of sintering tests on CeO_2–TZP-based materials containing 20 mol % CeO_2. We noted that samples prepared with mechanically alloyed powders reached very low density values even after quite long soaking times at high temperature. We suggested densification may be retarded by the wide particle distribution and by the extreme reactivity of the crystallites, which form agglomerates with an elevated porosity at low temperature. However, a wide particle distribution can be restricted both by wet milling or by flo-deflocculation, which also have a strong influence on the reactivity of powder particles.

Also, in the present work, MA° powders are highly reactive because mechanical alloying is carried out on powders containing electrostatically charged particles, and impacts between the spheres, particles and jar multiply the number and total amount of charges (as milled powders are attracted by a glass rod). The particles can consequently form large and soft lumps even at room temperature. We may hypothesize that the contraction of MA° samples at about 300 °C is caused by the sudden loss of electrostatic charge. As the electrostatic repulsion forces disappear, particles can move closer to each other, denser originate clots and samples contract.

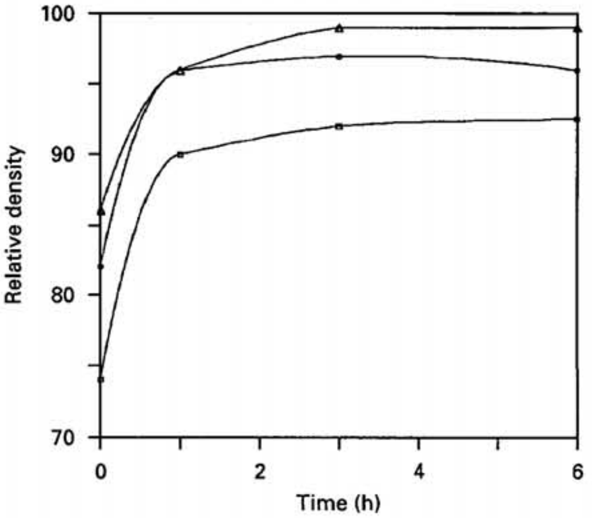

Figure 6 Relative density versus sintering time at 1450 °C: ○, CP = coprecipitated, □, MA° = mechanically alloyed, △, MA′ = mechanically alloyed and flo-deflocculated. The zero point corresponds to the density of samples sintered 1 min at 1450 °C.

Flo-deflocculation breaks down many of the largest agglomerates and electrically stabilizes the smallest particles, thus improving the global sample densification. At the same time, agglomerates disperse into finer particles as a result of electrical repulsion forces in an acid environment, but floc in a basic environment to form more compact agglomerates with reduced porosity: specific surface area decreases and green density increases.

Powders prepared by coprecipitation contain small particles, porous agglomerates and large irregular aggregates grown during calcination and not broken by the subsequent milling process. This complex morphology causes a high specific surface area and a relatively low density of the green samples.

Sintering tests demonstrated that sinterability of powders produced by these methods is not only a function of surface area, because a factor of two difference in the surface area of the mechanically alloyed powders leads to a significant difference in the sintering behaviour. In fact the surface area difference would suggest that the flo-deflocculated powder having the smallest surface area would perhaps have the lowest sintering density, whereas we have observed the highest. Therefore, a higher dependence on agglomerate or aggregate distribution as well as from crystallites reactivity seems reasonable. Moreover, it has been demostrated that large agglomerates retard sintering while large and irregular aggregates (> 100 μm) do not. We can therefore suppose that large aggregates are not so deleterious as agglomerates.

It must be also pointed out that crystallite dimensions have an influence on the grain size of sintered materials. In fact, materials obtained from coprecipitated powders, which have an average crystallite size of 30 nm, have grains of 1.5 μm after 3 h at 1450 °C; those prepared with mechanically alloyed powders, which have an average crystallites size significantly lower (10 nm), have average grain sizes of 0.5 μm (MA°) and 0.8 μm (MA′), respectively.

4. Conclusion

Powders prepared by coprecipitation, mechanical alloying and flo-deflocculated mechanical alloying have different sintering behaviour. Samples of the first type reach a high density after 3 h at 1450 °C, whereas mechanically alloyed samples, which have finer grains, do not.

The flo-deflocculation route reduces the agglomerate size of powders prepared in this way and improves sinterability so that specimens can reach densities close to theoretical values.

Crystallite dimensions seem to have a strong influence on the grain size of sintered materials. Powders produced by the chemical method have an average size of 30 nm and samples having a grain size of 1.5 μm after 3 h at 1450 °C were obtained. On the other hand, materials with a finer microstructure can be produced with mechanically alloyed powders, which have a much smaller crystallite size (10 nm).

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