

# Innovative Milling of Ceramic Powders: Influence on Sintering Zirconia Alloys

G. Farnè,<sup>a\*</sup> F. Genel Ricciardiello,<sup>b</sup> L. Kucich Podda<sup>c</sup> and D. Minichelli<sup>d</sup>

<sup>a</sup>ISTIC, via Opera Pia, 16143 Genova, Italy

<sup>b</sup>DICAMP, via A. Valerio 2, 34127 Trieste, Italy

<sup>c</sup>DIMCA, via A. Valerio 2, 34127 Trieste, Italy

<sup>d</sup>DSTC, via Cotonificio, 33100 Udine, Italy

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## Abstract

The preparation of zirconia alloys precursors was carried out by several different methods to reduce firing times and sintering temperatures. Innovative milling processes such as mechanofusion (MF) and mechanical alloying (MA) were introduced on powders prepared from traditional oxides and from pyrolytic precursors. In order to evaluate the effect of innovative milling systems, the powders and related sintered bodies were characterized by XRD, SEM, EDAX and DSC techniques. © 1999 Published by Elsevier Science Limited. All rights reserved

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## 1 Introduction

The sintering of ceramics is a critical process. To obtain materials with controlled porosity and density an important step is the choice of the starting powders preparation process. These preparations can be made in different ways and a wide related bibliography is available.

Among the different processes, the authors proposed the pyrolysis of some soluble salts. The precursors preparation was optimized for several ceramics: as for example, alloys based on ZrO<sub>2</sub>–CeO<sub>2</sub>–Y<sub>2</sub>O<sub>3</sub>,<sup>1,2</sup> microwave ceramics<sup>3</sup> and superconductors as BSCCO.<sup>4</sup> In all these products, the final materials appeared suitable for electrical and electronic applications and the sintered products showed higher properties than those of traditional ones.

The pyrolytic powders were homogeneous and highly reactive, but, owing to their small particle size, exhibited a grain agglomeration with a typical plate-size morphology, which is not good for high quality forming processes. To obtain well sintered materials a further calcination step was necessary, but by this process an increase in the particle size was introduced with a subsequent, undesired decrease in powder reactivity.

An attempt, to break the plate-size powder clusters and therefore to enhance the characteristics of the sintered bodies, was performed introducing a step of innovative milling. In the present investigation mechanical alloying (MA) and mechanofusion (MF) milling systems were used. These procedures are common in metallic powder metallurgy, but quite unusual for ceramic powders. The material chosen for experimental work is a zirconia–ceria–yttria alloy, proposed for oxygen sensors and MHD systems and previously investigated by the authors.<sup>2,5,6</sup>

## 2 Experimental

### 2.1 Sample preparation

The composition of zirconia alloy tested in this investigation was 40 mol% ZrO<sub>2</sub>, 40 mol% CeO<sub>2</sub> and 20 mol% Y<sub>2</sub>O<sub>3</sub>. Three different powders were prepared with this composition. First, powder oxides (Fluka AG) were weighted and milled with water in agate mortars and agate ball mill, in a traditional way. This method was used in a previous work<sup>7</sup> and the obtained precursors required high sintering temperature and prolonged time for a good sintering (porosity lower than 5%).

The other powders were prepared by pyrolysis according to a previously described procedure.<sup>2,3</sup> Soluble salts of Fluka yttrium nitrate hydrate, Fluka zirconium acetylacetonate and Strem cerium acetate, were dissolved in water with dilute nitric

\*To whom correspondence should be addressed. Fax: +39-10-3632586; e-mail: genel@dicamp.univ.trieste.it

acid. A chelating agent solution (citric acid for the second preparation and tartaric acid for the third) was added under stirring at 80°C, to this solution, and pH was controlled by a dilute ammonia solution, to reach the required value of 5–6. In this conditions, the pyrolysis was carried out in an open stainless steel vessel: the solution was heated and concentrated until a rise of a light flame indicated the starting of pyrolysis and soft powders grown up until the end of process.<sup>7</sup>

## 2.2 Milling

The prepared precursors required a further process of calcination before firing. To avoid this step and the related grain growth, two different milling methods, mechanical alloying and mechanofusion, quite innovative in ceramics, have been applied.

Mechanical alloying (MA) is a method for powder comminution obtained by the repeated fracturing and rewelding of powder particles in a highly energetic ball charge.<sup>8,9</sup> In this investigation the process was performed in a modified Retsch planetary mill. Each of the cylindrical tempered steel containers was loaded with 4 balls (1 cm diam.), having a weight ratio balls/powder of 13:1. To avoid warming up during milling, the vials were cooled by forced air flow in an alternate milling and rest times of 10 min. The mechanofusion (MF) system, manufactured by Hosokawa Micron Corp., consisted of a high-speed rotating chamber and a scraper: the powder loaded in the chamber was pressed on the inside walls by centrifugal forces; during this process various forces are applied such as compression, attrition, shearing and rolling. The different powder preparations are summarized in Table 1.

## 2.3 Firing of the samples

All the processed powders were pressed at 2000 Kg/cm<sup>2</sup> into disks 1×1 cm and then sintered at 1400°C for 200 h in a tubular furnace in oxidizing atmosphere. The firing parameters have been chosen on the basis of previous investigations,<sup>7</sup> to reach equilibrium conditions.

## 2.4 Powders characterization

The prepared and treated powders were characterized by XRD. The analysis was carried out by a Philips goniometer, using Cu K<sub>α</sub> radiation and a scanning speed of 1/2θ min. In Fig. 1 the X-ray diffraction diagrams of the citrate and tartrate powders are compared with those of sintered samples: the formation of a fluorite-type solid solution, even poorly crystallized, for the pyrolytic powders was clearly evidenced.

The starting powders were also investigated by means of a Philips SEM attachment and the results are showed in Figs 2 and 3; it is clearly evidenced the agglomeration of quite small grains that was not completely destroyed even after prolonged milling times. On all the milled powders the EDAX

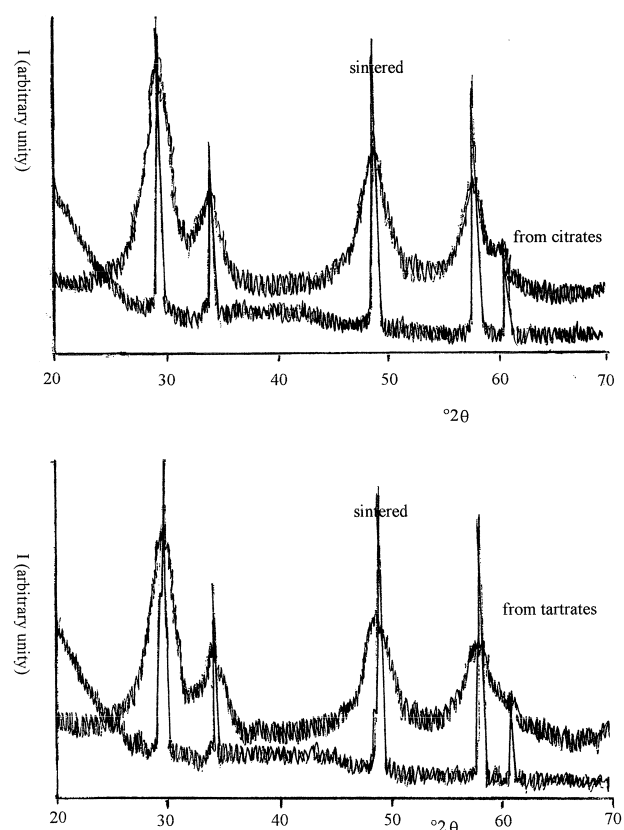


Fig. 1. XRD of pyrolytic powders.

Table 1. Preparation methods for the samples

Sample	Powder preparation	Powder treatment	Treatment conditions
1	Citrate pyrolysis	Mechanical alloying	0.5 h, 250 rpm
2	Citrate pyrolysis	Mechanofusion	0.5 h, 10 rps
3	Citrate pyrolysis	Mechanical alloying	5 h, 250 rpm
4	Citrate pyrolysis	Mechanofusion	5 h, 10 rps
5	Mixing and milling	Mechanical alloying	0.5 h, 250 rpm
6	Mixing and milling	Mechanofusion	0.5 h, 10 rps
7	Mixing and milling	Mechanical alloying	5 h, 250 rpm
8	Mixing and milling	Mechanofusion	5 h, 10 rps
9	Tartrate pyrolysis	Mechanical alloying	0.5 h, 250 rpm
10	Tartrate pyrolysis	Mechanofusion	0.5 h, 10 rps
11	Tartrate pyrolysis	Mechanical alloying	5 h, 250 rpm
12	Tartrate pyrolysis	Mechanofusion	5 h, 10 rps

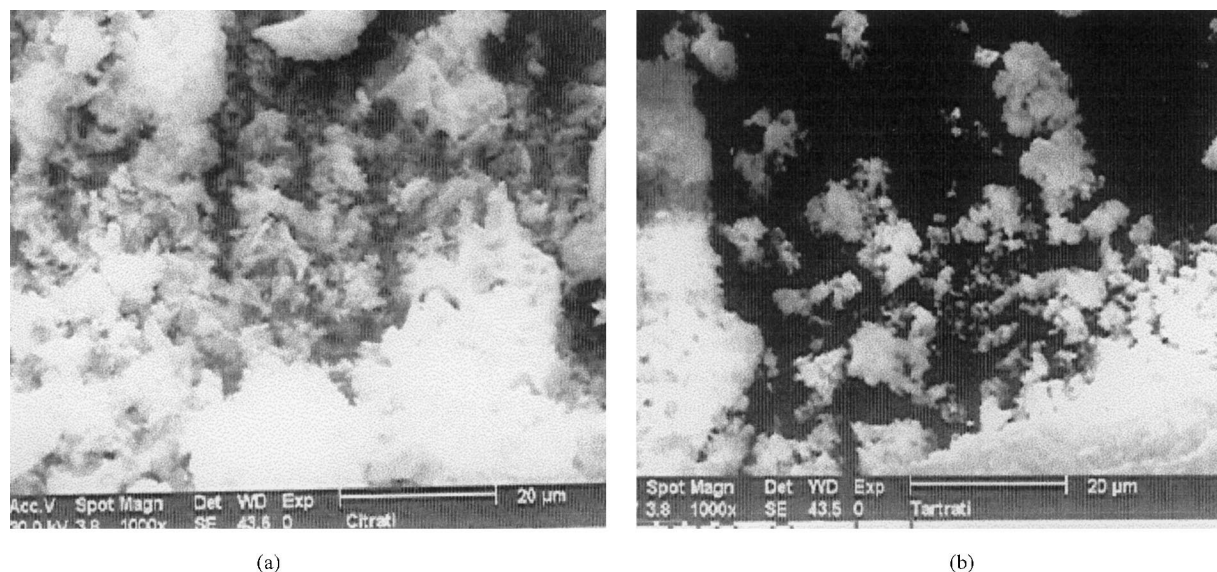


Fig. 2. Pyrolytic powders (a) from citrates, (b) from tartrates.

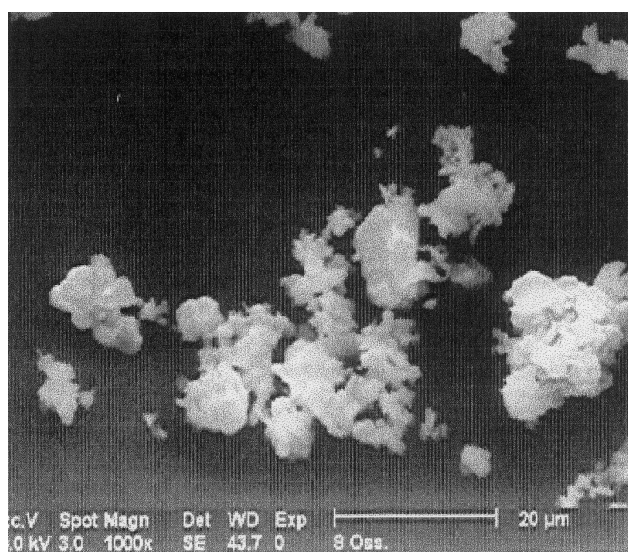


Fig. 3. Milling and mixing powders.

analysis showed the absence of metals as iron and cobalt and therefore no pollutants have been introduced in these precursors after the innovative milling processes.

Finally, a Setaram DSC was used for investigation at the following conditions: temperature range 20–450°C, heating rate 5°C/min and Al crucibles. The results are summarized in Table 2 and the most significant plots are reported in Figs 4 and 5.

### 2.5 Sintered samples characterization

The sintered samples were characterized by XRD and SEM techniques and by porosity determinations.

In all the samples the presence of the well crystallized fluorite-type solid solution was clearly evidenced by XRD.

Table 2. DSC data obtained on the powdered samples

Sample	$T_{min}$ (°C)	$T_{max}$ (°C)	$\Delta H$ (J/g)	$T_g$ (°C)
1	118	314	−89	
2	94	330	−108	
3	110	315	−97	
4	89	340	−132	
from citrates (starting powders)	244		+17	
5		182	−0.5	
6	56	291	−1.1	
7		184	−0.5	272 389
8		159(I)	−3.3	284
		190 (II)	−1.4	
mix and mill (starting powders)	no effect			
9	93	232	+138	
10		293	+181	
11		207	+129	
12		282	+160	
from tartrates (starting powders)		287	+45	

$T_{min}$ —temperature of the first effect,  $T_{max}$ —temperature of the second effect,  $T_g$ —temperature of slop variation in the curve.

- SEM: all the sintered samples were examined in the same conditions used for the powders and the related micrographs are reported in Fig. 4–6.
- Density determination: the apparent densities were determined by a picnometric method and the theoretical density was calculated by XRD data. The values of the apparent densities and of the porosity are summarized in Table 3.

### 3 Results and Discussion

The introduction of innovative ceramic powders milling systems as MA and MF did not give pol-

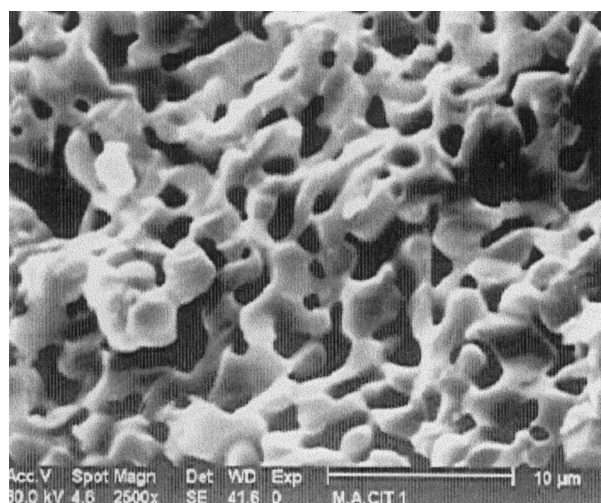
lution in the products: all the performed SEM/EDAX analyses did not show any traces of elements such as Fe, Co and Cr present in the steel milling attachments. It was suggested that the constitution of a protective powder layer on the mill walls prevented contamination.

All the mean phases present both in the starting powders and in the sintered samples were identified by XRD: in all the considered samples, obtained both by pyrolytic precursors and by traditional oxides, the unique phase detected in the sintered specimens by XRD was the fluorite-type solid solution (Fig. 1). Further SEM powder analyses showed a partial deagglomeration of the milled powders with the formation of primary particles strictly similar each others (Figs 2 and 3). Further, DSC examinations of the same specimens showed that the starting powders obtained by traditional oxides did not exhibit thermal effects (Table 2); on the contrary, all the precursors showed an exothermic peak at about 250°C (Figs 7 and 8). Other noteworthy effects, detected by DSC

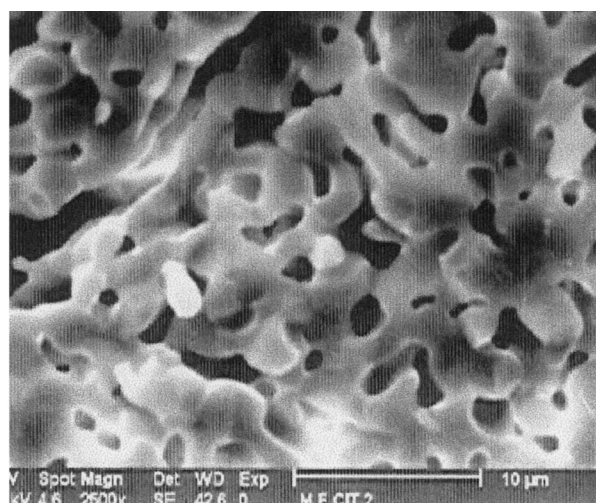
**Table 3.** Experimental apparent density and calculated porosity of samples

Sample	Apparent density (g/cm <sup>3</sup> )	% Porosity
1	—	—
2	4.860	15.2
3	5.169	9.8
4	4.894	14.6
from citrates (starting powders)		
5	5.033	12.2
6	4.522	21.1
7	5.288	6.2
8	—	—
mix and mill (starting powders)		
9	5.225	8.8
10	4.798	16.3
11	5.428	5.3
12	4.868	15.0
from tartrates (starting powders)		
		4.9

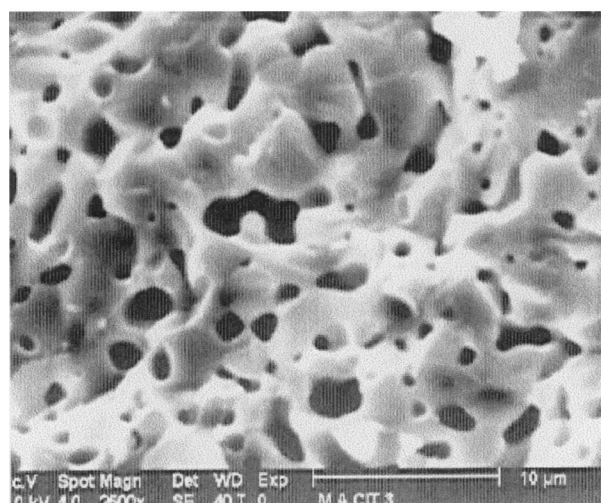
Theoretical (bulk) density for the alloy (from XRD data): 5.728 g/cm<sup>3</sup>



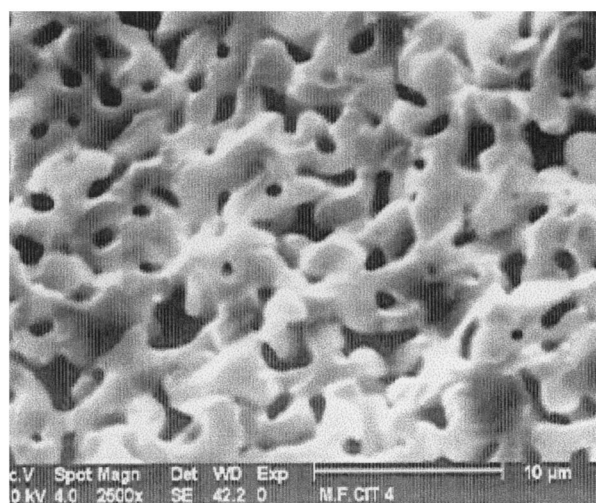
(a)



(b)



(c)



(d)

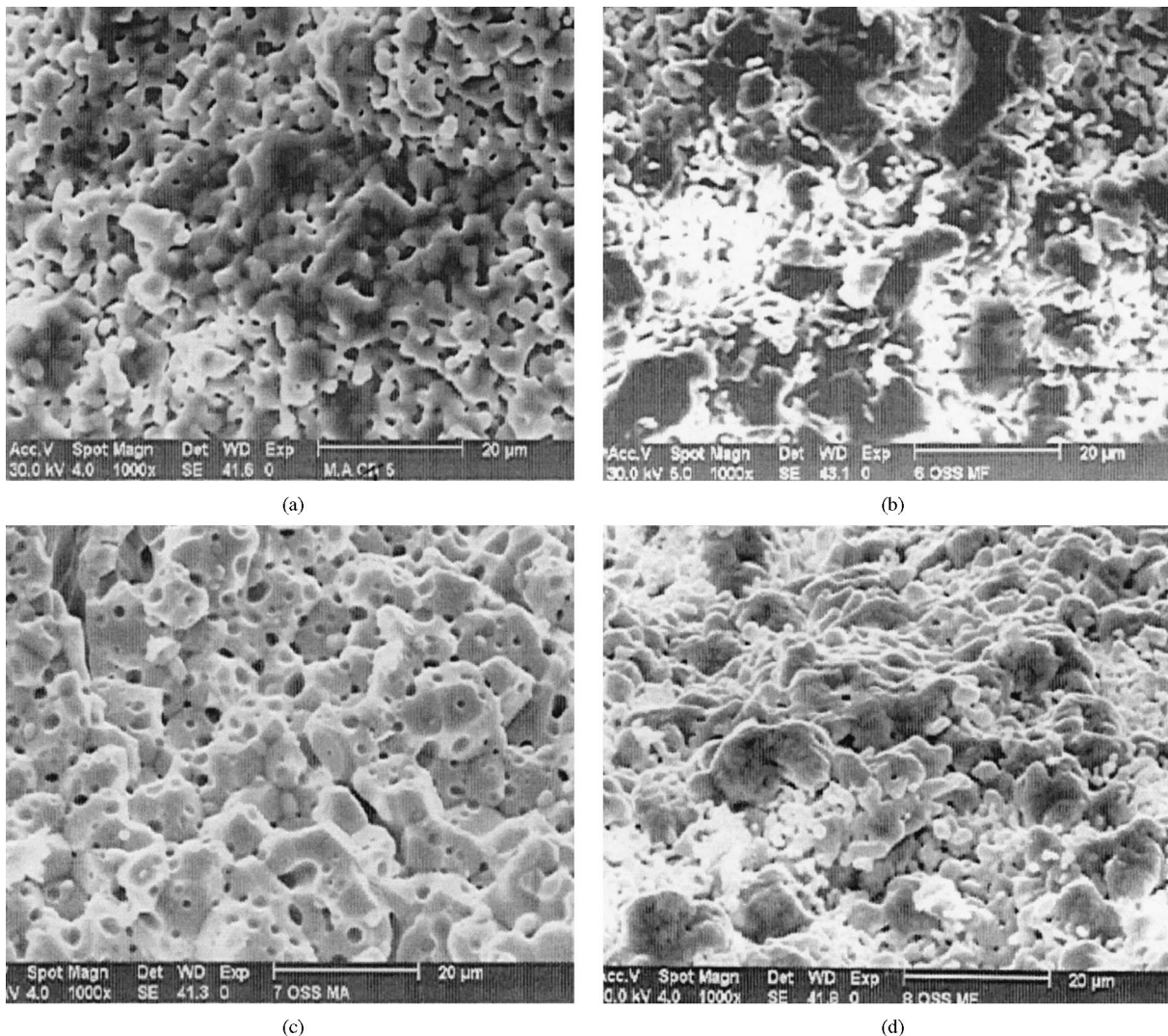
**Fig. 4.** Sintered samples from citrates: (a),(c) milled by MA; (b),(d) milled by MF.

on the milled starting powders, can be summarized as follows:

- the traditional powders showed a low enthalpy endothermic effects, with the presence of strong variations of the peaks slopes in the samples milled for prolonged times (Fig. 7);
- the precursors obtained by citrates pyrolysis showed endothermic effects at about 320°C, while the ones obtained by tartrates showed exothermic effects at about 250°C (Fig. 8);
- the enthalpy values obtained on the milled powders were always greater for the MF treated powders, whatever was the previous history of the samples. This phenomenon, no interpretation of which could be advanced, is probably correlated to the greater porosity values exhibited by all the sintered samples whose starting powders revealed greater enthalpy values.

The powder parameters (as particles size, surface area and so on) affecting the densification process

during sintering were then taken in account: however, considering that all the samples showed the same compositions, the bulk parameters as diffusion coefficients and lattice defects were not considered as suggested strictly similar in all the specimens. The observed DSC thermal effects could be correlated to a grain softening for the milled powders: these grains seem to be heavily stressed, but not broken by milling. Since the thermal analyses were conducted at low temperatures, it could be suggested that the energy introduced on the powders by mechanical stresses could have been exhausted at low temperatures, when the diffusion at solid state can be considered near zero; assuming this hypothesis, a high porosity in the sintered samples could be observed and accepted. This phenomenon is undoubtedly particular, since stressed powders are expected to be strongly reactive aiming to yield dense sintered materials. In this case, an uncommon densification process could be suggested, as showed by SEM micrographs (Figs 4–6).



**Fig. 5.** Sintered samples from traditional powders: (a),(c) milled by MA; (b),(d) milled by MF.

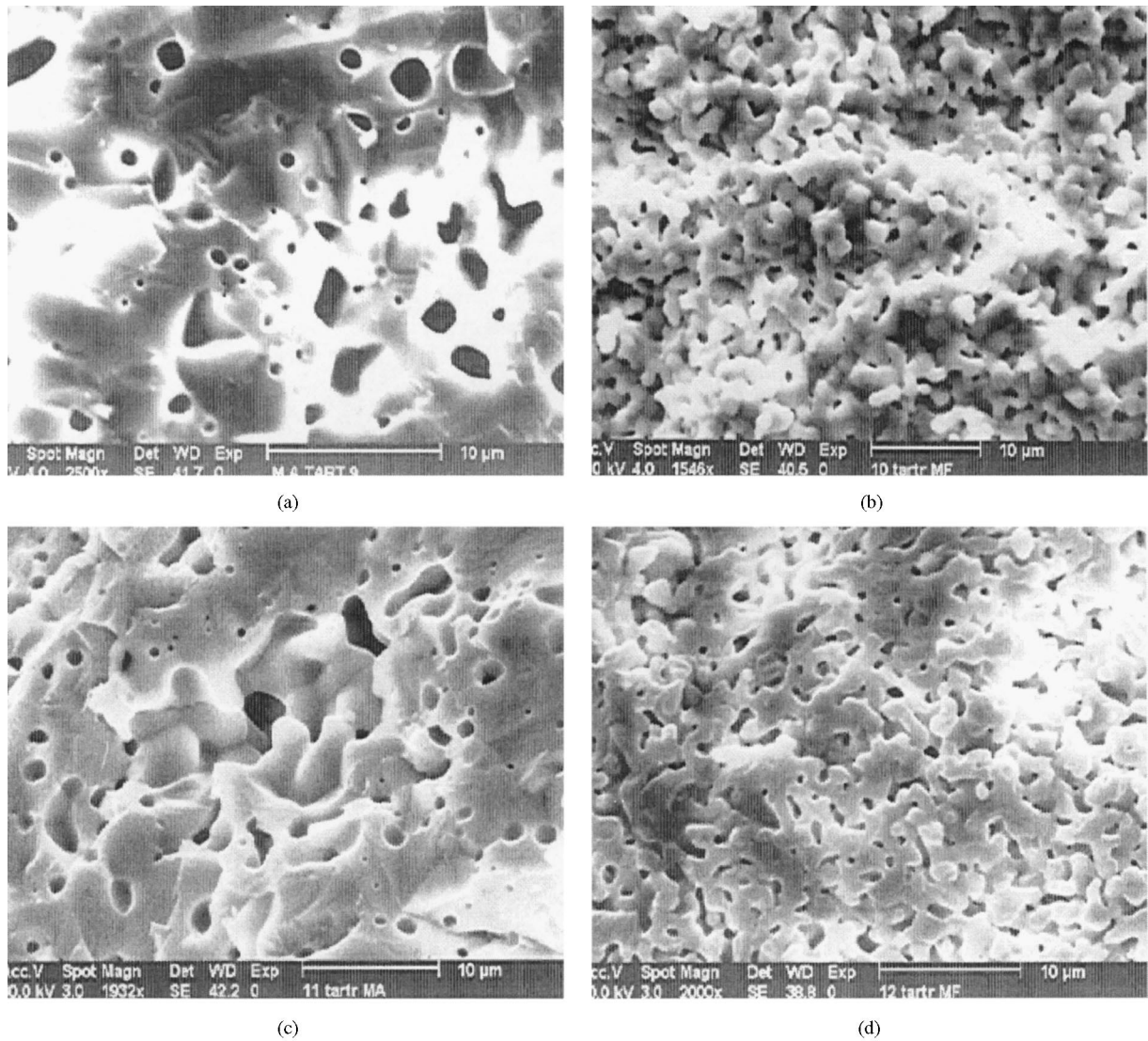


Fig. 6. Sintered samples from tartrates: (a),(c) milled by MA; (b),(d) milled by MF.

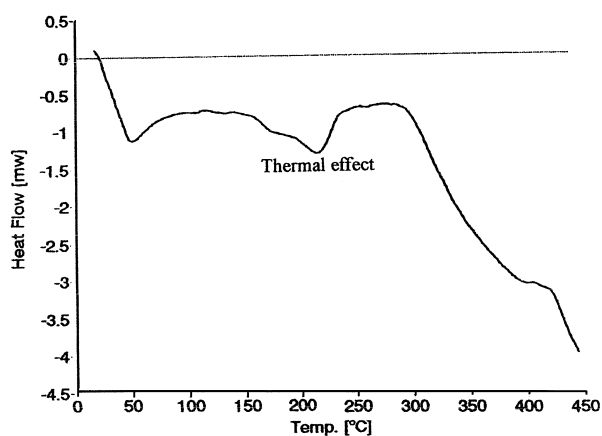


Fig. 7. Heat flow versus  $T$  for the sample 8.

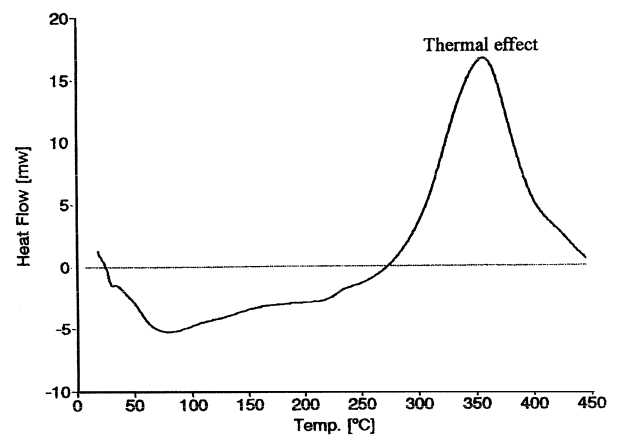


Fig. 8. Heat flow versus  $T$  for the sample 10.

The observed rounded grain borders could not be explained in terms of liquid phase presence, as this fact should have given not porous sintered products: in addition, the samples were fired for prolonged times at temperatures well below the presence of liquid phases, as showed by the phase

diagrams relative to the systems  $ZrO_2-CeO_2-Y_2O_3$ .<sup>5,10,11</sup>

It was therefore necessary to suggest a densification mechanism well distinct in two different parts: in a first time, at low temperatures, a first rearrangement of the grains could be happened with

subsequent rounding and growing of the powders grains (this effects can be due to the presence of severe stresses present after innovative milling which were dissipated at temperatures too low for giving diffusion and recrystallization effects); a further sintering process could be happened in a traditional way, maintaining the high porosity and the large grain sizes present in the mass.

The porosity measurements confirmed these considerations and put in evidence that the innovative milling processes, both MA and MF, deleted the previous histories of the powders.

In practice, all the powders yielded sintered products having similar, low porosity, clearly evidenced from Figs 4–6.

It is noteworthy to observe that previous works have pointed out the difficulty of sintering these materials by traditional processes,<sup>2</sup> owing to the morphology of the starting powders.

#### 4 Conclusions

Both MA and MF innovative milling systems for ceramic powders gave unpredictable effects for the investigated alloy: the previous histories of the powders were deleted and a great lot of pores, both intra- and intergranular, were originated. In all the specimens, rounded grains borders with high porosity were observed after milling treatments and firing processes (Figs 4–6). A tentative way to explain this phenomenon was tried suggesting that the strong mechanical stresses introduced in the materials by MA and MF systems were absorbed at low temperatures, as seen by DSC (Figs 7 and 8).

The successive high temperature firing of these powders kept constant the shape of the grains and the porosity introduced at lower temperatures: these effects appeared very interesting and will be object of further investigations.

In short, some considerations can be summarized as follows:

- both MF and MA systems gave similar sintered products, whatever could be the preparation cycle of the powders (traditional

oxides, pyrolyzed precursors) with no metal particles pollution;

- all the sintered products appeared largely porous, above all the samples prepared after MF milling process; these products seem to be interesting for all the cases where a high surface area can be requested (gas sensors);
- the border grains of the sintered materials appeared rounded, as introduced by the strong mechanical stresses induced by milling systems, with a complete deleting of the preparation history of the powders.

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