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SPRING COLLEGE IN MATERIALS SCIENCE
ON
'CERAMICS AND COMPOSITE MATERIALS'
(17 April - 26 May 1989)

SINTERING AND MICROSTRUCTURES
(Lecture III)

Sergio MERIANI
Istituto di Chimica Applicata e Industriale
Università di Trieste
34127 Trieste
Italy

DILATOMETRY SINTERING STUDIES

SINTERING is studied by DENSITY/POROSITY evaluation but actual IN SITU measurements of SHRINKAGE can be detained only by dilatometry.

Theory: sintering is an activated process - Several eq. describe different stages but none of these can be exactly related to the "OVERLAPPING" process which take place in a "REAL" powder when it undergoes a "HEATING CYCLE"

The approach can be either

ISOTHERMAL
Fixed (T) Temp.

ISOCHRONAL
Fixed (dT/dt)

1) ISOTHERMAL

The following equation has been generally used

$$\boxed{Y = \frac{\Delta L}{L_0} = (k(T)\,t)^n = \left[\left(Z \exp\left(-E/RT\right)\right)t\right]^n}$$

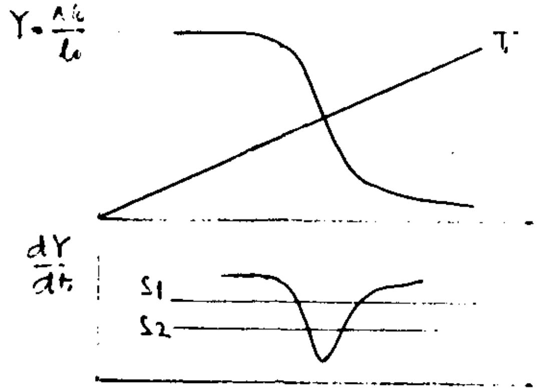
ΔL = shrinkage	L_0 = initial length
k = Arrhenius const.	n = kinetics factor
Z = pre.exp factor	E = activation energy
t = time	T = temp

Plots $\log \frac{\Delta L}{L_0}$ vs $\log t$ should give straight lines, slope "n" related to sintering mechanism.-

The system requires time and lots of samples.

1-a QUASI-ISOTHERMAL DILATOMETRY "QID"

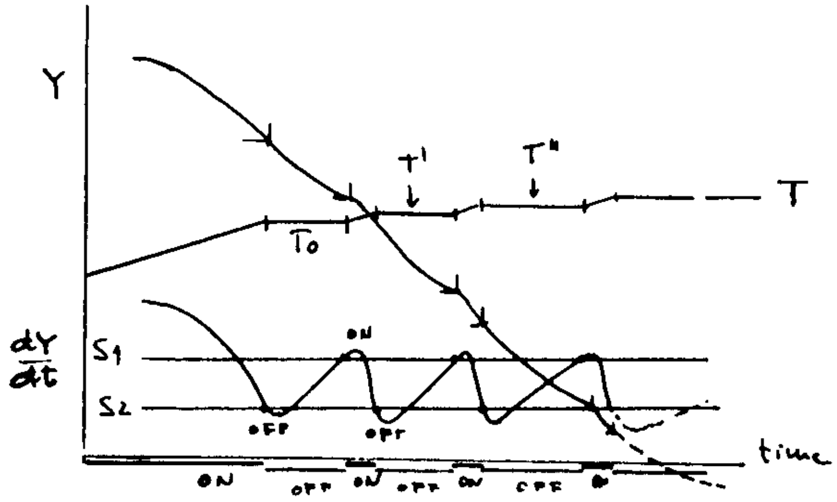
It is based on the monitoring of the DERIVATIVE signal of the SHRINKAGE during the regular heating ramp.



shrinkage at a constant heating rate

Shrinkage rate

PRINCIPLE OF QUID



when $dY/dt < S_2$ heating is SWITCHED TO CONSTANT
" " $> S_1$ " " RESUMED

There are several ISOTHERMAL steps which could be treated as previously!

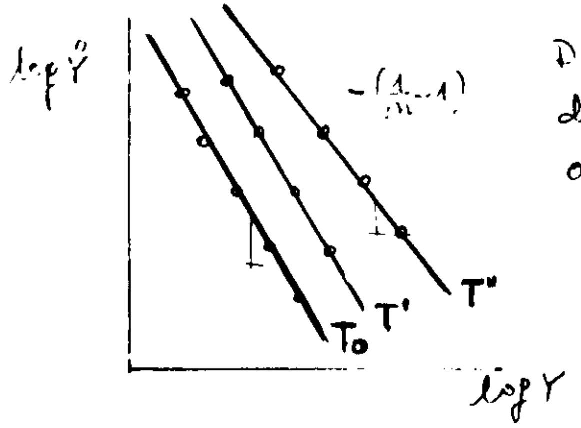
QUID equations

$Y = \frac{\Delta L}{L_0} = k(T)\, t^n$ taking the "time" derivative

$\frac{d}{dt}\left(Y^{1/n}\right) = k(T)\, t \qquad \frac{1}{n} Y^{(1/n-1)}\left(\frac{dY}{dt}\right) = k(T) \qquad \overset{\circ}{Y} = \frac{dY}{dt}$

$\overset{\circ}{Y} = n\, k(T)\, Y^{-(1/n-1)}$

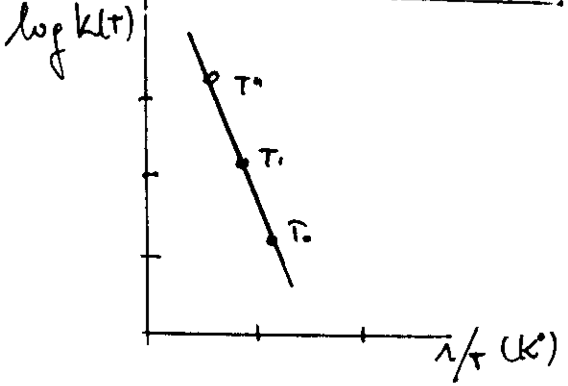
$$\boxed{\log \overset{\circ}{Y} = \log n + \log k(T) - (1/n - 1)\log Y}$$



Different slopes are due to different "n" overall mechanisms

Being $\log k(T) = \log\left[Z \exp(-E/RT)\right]$

$$\boxed{\log k(T) = \frac{-E}{R}\frac{1}{T} + \log Z}$$



In case of CeO2/ZrO2

$E = 103.5$ Kcal/mol

$n = 0{,}3$ (?)

'ISOCHRONAL' fixed heating rate dT/dt

If we assume a constant HEATING RATE ϕ

$\frac{dY}{dt} = k(T)\, Y^m \qquad \frac{dY}{dt} = Z \exp(-E/RT)\, Y^m$

if $\phi = \frac{dT}{dt}$ then $\frac{dY}{dT} = \left(\frac{dY}{dt}\right)\left(\frac{dt}{dT}\right) = \frac{Z}{\phi} \exp(-E/RT)\, Y^m$

$\frac{d^2Y}{dT^2} = \frac{Z}{\phi} \exp(-E/RT)\left[n Y^{n-1}\left(\frac{dY}{dT}\right) + Y^n\left(\frac{E}{RT^2}\right)\right]$

The second derivative is "0" at the inflexion point "i" of the shrinkage curve. Therefore at Ti

$0 = n Y^{n-1}\left(\frac{dY}{dT}\right) + Y^n\left(\frac{E}{RT^2}\right)$

then $\boxed{E = -nRT_i^2\, Y_i^{n-1}\left(\frac{dY}{dT}\right)_i \cdot Y_i^{1/n}}$

where T_i, Y_i and dY/dT are the variables at the point "i" ....

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REFERENCES

QUID O.T. SØRENSEN J. Therm. Anal 13 (1978) 429
" " Thermochimica Acta 29 (1979) 211

ISOCHRONAL { Y. TOMITA J. Mat Science 24 (1988) 731
CG GENUIST, et Al Ceramics Int 14 (1988) 169

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Experimentals → SLIDES

SINTERING AIDS FOR Ce-TZP

S. Maschio*, E. Bischoff°, O. Sbaizero*, S. Meriani*

*Istituto di Chimica Applicata e Industriale
Università di Trieste - ITALY

°Max Planck Institut fur Metallforschung
Institut fur Werkstoffwissenschaften
Stuttgart - F.R. GERMANY

ABSTRACT

Ceria-stabilized zirconia seems to become as interesting as the more studied yttria-zirconia system. Its critical grain size is larger and it does not undergo low temperature moisture degradation; but still its grain size control remains very important because the mechanical properties are strongly influenced by the size of the tetragonal grains.
In this work additives for the pressureless sintering of Ce-TZP, have been studied. The temperature at which the shrinkage begun did not decrease using MnO_2 or CuO, but at the same temperature the sintering rate was higher; MnO_2 and CuO were also very effective in improving both the tetragonal phase content retained at room temperature and the mechanical properties (hardness, bending strength and toughness)

1. INTRODUCTION

The ceria-zirconia system is being developed as an alternative to the more investigated yttria-zirconia because of its better performance in a moist environment[1], its lower price, the wider range of solubility in ZrO_2 and the very good mechanical properties[2]. Furthermore it is interesting for the presence of two tetragonal phases[3] which might give an additional improvement to the mechanical properties through crack deflection mechanism.

Unfortunately the use of CeO_2 showed a limited sinterability and even the use of expensive methods like hot- or hot-isostatic pressing to fully densify the poor sinterable material were not suitable because Ce is reduced from Ce^{+4} to Ce^{+3} during the process and zirconia undergoes the tetragonal (t) to monoclinic (m) transformation.

The aim of this investigation is to find out the effectiveness of additives (CuO, MnO_2) for the sintering of Ce-TZP according to a pressureless process, keeping in mind that in order to get outstanding mechanical properties the material must contain almost 100% of tetragonal phase and the density must be as close as possible to the theoretical density to avoid the presence of defects which may provide easy routes for crack initiation.

2. METHODS

0.05 M solution of $CeCl_3 \cdot nH_2O$ was used as starting material.
Cerium carbonate was precipitated by adding urea and then boiling the solution for 3 hrs. The white salt was washed with H_2O, dried and calcined at 750 °C.

The resulting oxide was granulated through 75 µm screen and mixed with ZrO_2 supplied by Toyo Soda in order to give a 12 mol% CeO_2-TZP.
The powders were mixed and homogenized by the flo-deflocculation route[4] using HCl for acidification and NH_3 solution for flocculation at pH 8. After flocculation the clear supernatant was removed and the wet powder was washed several times using distilled water, then dried.
In order to study the influence of additives on the sinterability, the dried Ce-TZP powder was divided in three sets:

- As-fabricated powder, labelled Ce-TZP
- As-fabricated powder + CuO (0.3 mol%), labelled Ce-TZP+Cu
- As-fabricated powder + MnO_2 (0.3 mol%), labelled Ce-TZP+Mn

Powders were ball milled 30 hrs with binder and lubricant, dried, granulated through 75 µm screen, uniaxially pressed at 200 MPa to form pellets 10 mm in diameter.
The green compacts, about 45% of the theoretical density, were sintered in air at 1450 and 1530 °C, respectively, for various periods of time.
Dilatometric tests were performed with a Netzsch dilatometer in air and oxygen, with a heating rate of 10°K/min.
The following measurements were made on the sintered bodies:
Archimede's method to measure densities,
X-ray diffraction for phases identification and the Garvie and Nicholson method[5] to assess the tetragonal to monoclinic ratio,
SEM pictures and the intercept method to estimate the average grain size,
SEM and TEM analysis to examine the microstructure as well as the additives' influence.
Modulus of rupture measurements were made using a 4-point bend jig with 30 mm outer span, 10 mm inner span and a cross-head speed of 0.1 mm/min.
Hardness was measured by Vicker's indentation with loads ranging from 90 to 200 N
The fracture toughness was measured by indentation strength in bending (ISB) technique using a Vicker's indenter, applying 200 N load, then breaking the specimen by the 4-points bending test above described.

3. RESULTS AND DISCUSSION

Fig. 1 shows the sintering plots for the different powders. They behaved in the same way as regards the thermal expansion of the pressed samples.

Moreover the onset shrinkage temperature, 1120 °C, remained unchanged by the addition of either Cu or Mn but the powders behaved differently after the initial shrinkage stage; the Ce-TZP displayed a two step densification (at 1220 °C) whereas powders with either CuO or MnO_2 densified in a single step. SEM analysis on Ce-TZP samples fired at 1220 °C revealed that the particles were already sintered leaving large intergranular voids which were difficult to eliminate hindering further densification. Continuing the heating it is possible to increase the shrinkage but at the same time anomalous grain-growth takes place.

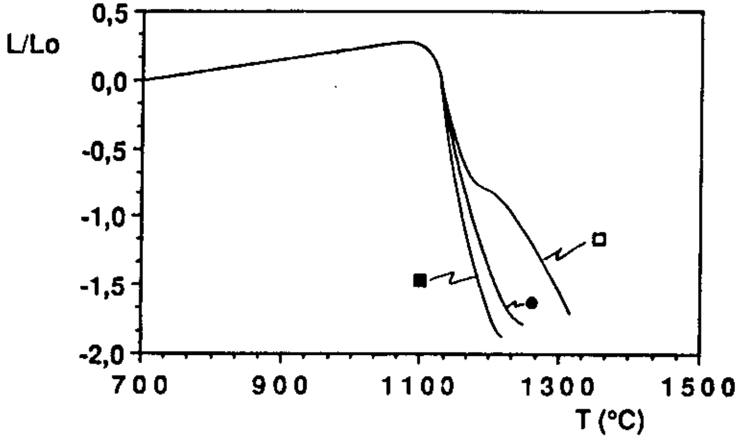

Fig. 1 Dilatometric curves for the different starting powders, (□) Ce-TZP, (■)Ce-TZP+Cu, (●) Ce-TZP+Mn.

Densification curves for the pressureless sintering in air at 1450, 1530°C are reported in Fig. 2, (separate samples were used to obtain the individual data points); the Ce-TZP compact required very high temperature and long time to reach good density while either CuO or MnO_2 additions enhanced densification as well as the amount of tetragonal phase retained at room temperature. CuO had the strongest effect whereas MnO_2 was slightly less effective but both remarkably changed the amount of tetragonal phase i.e. after 2 hours at 1450 °C a fully tetragonal body could be obtained.

From the Fig. 2 it is possible to see that for samples sintered either at 1450 or 1530°C the maximum in the density was reached after 4 hours at 1450 and 2 hours at 1530°C, afterwards the amount of tetragonal phase increased (in the case of undoped material) but the density slightly decreased.

Fig. 3 shows the grain growth kinetics of Ce-TZP, for a constant temperature, with and without dopants, it can be seen that over the range of time considered samples without dopants had a grain size about twofold larger than those doped. For example in this log-log plot the slope for the Ce-TZP is 0.54, whereas for the Cu doped samples is 0.27 and for the Mn doped is 0.20.

The grain growth kinetics can be expressed as:

$$G^n(t) - G^n(0) = k\,t \qquad (1)$$

where G(t) is the grain size after sintering for time, t; G(0) is the grain size extrapolated for time t=0; k is a proportionality constant and n is the growth exponent. For Ce-TZP n≈1.9 whereas Cu and Mn dopants rose the growth exponent, n, to ≈3.5 and ≈4.5 respectively.

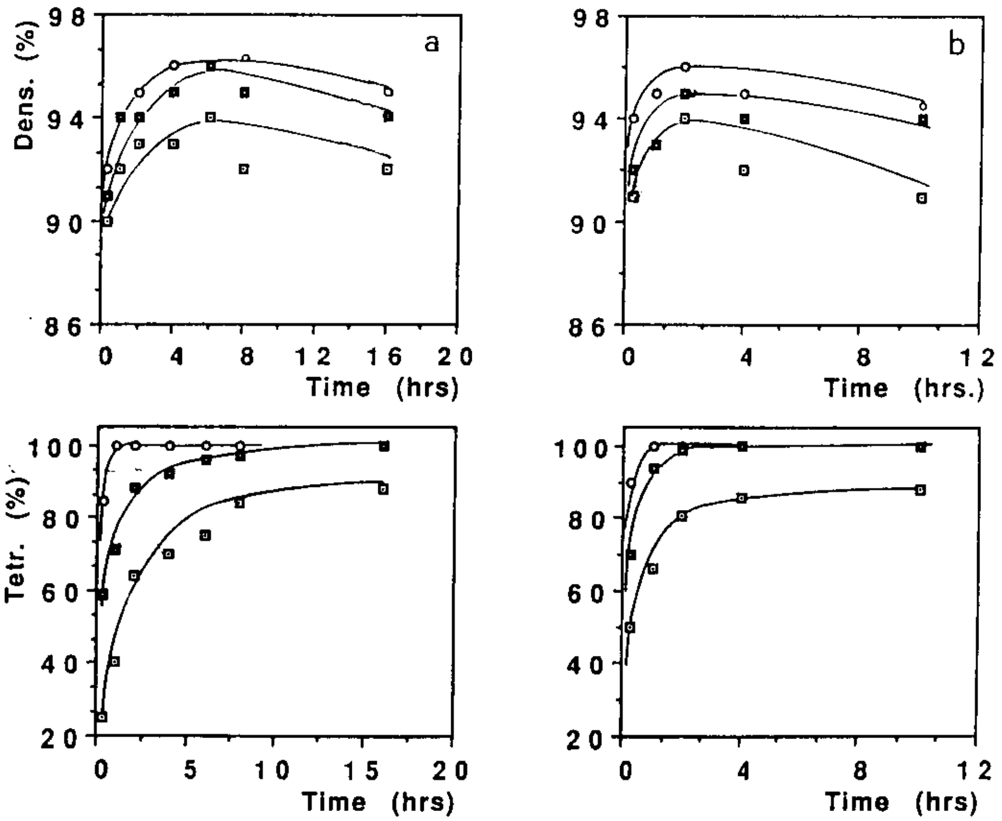

Fig. 2 Density and amount of tetragonal phase of sintered samples vs sintering time for: (a) 1450 °C, (b) 1530 °C, (⊡) Ce-TZP,(○)Ce-TZP+Cu, (▣) Ce-TZP+Mn.

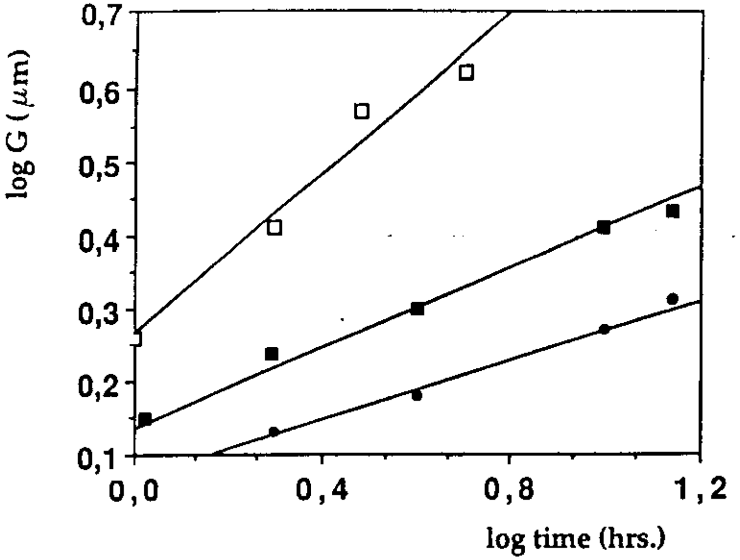

Fig. 3 Grain growth kinetics of Ce-TZP samples showed by log-log plot of grain size vs sintering time, (□) Ce-TZP, (●) Ce-TZP+Mn, (■) Ce-TZP+Cu

Fig. 4 shows the microstructure of samples sintered for 4 hours at 1530 °C, the resulting microstructure was made of fine and homogeneous grains 4-5 μm for Ce-TZP, 2 μm when CuO was used and 1.4 μm with MnO_2.

TEM analysis, Fig. 5, revealed the presence of liquid phase at the triple point grain boundaries (pockets) only when Cu was used due to the fact that CuO transforms into Cu_20 which then melts at 1236°C, whereas we were unable to spot Mn-reach areas. Therefore experimental results showed that under the same sintering conditions, small amounts of CuO could improve the sintering of Ce-TZP more effectively that MnO_2 but the latter was stronger in depleting the rate of grain growth. It is hard to explain the reasons of these different effects but the dopants influence on the densification should be discussed on the basis of the defect forming ability of the ions available after the first sintering stage common to both the pure and doped materials. Both CuO and MnO_2 undergo a high temperature reduction forming Cu_2O and $MnO_2 \cdot Mn_2O_3$ respectively. New ionic species like Cu^{+1} and Mn^{+2} become available at 1200°C to possibly interact with the sinter-reactive ceria and zirconia particles which, being both tetravalent, do not introduce oxygen vacancies in the crystal lattice.

It has been assumed that in stabilized zirconias the defect structure is fixed by the amount of the aliovalent stabilizers as Ca^{+2} and Y^{+3}. Any other dopant present in small quantity cannot possibly modify the defects' number and structure of the host matrix nor the lattice diffusion

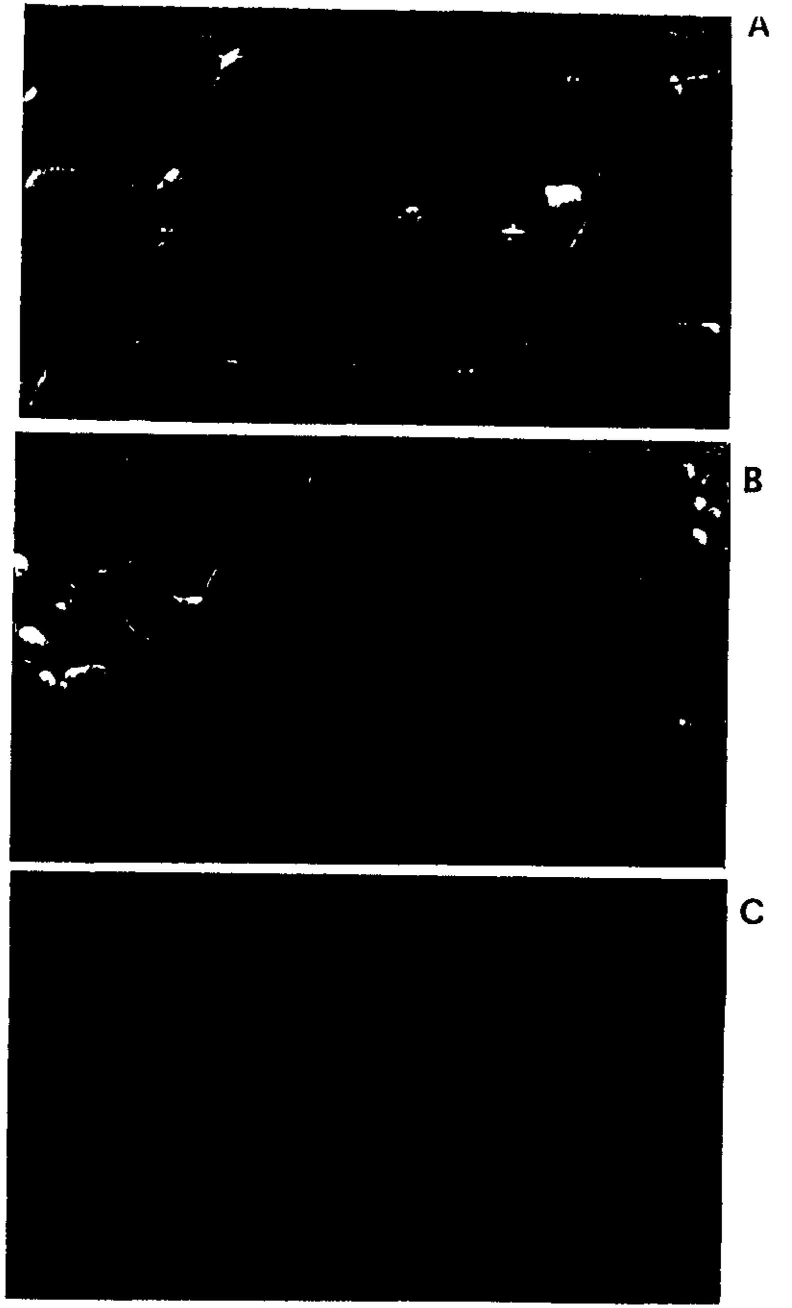

Fig. 4 SEM pictures of the Ce-TZP materials sintered at 1530 °C for 4 hours, (A) Ce-TZP, (B) Ce-TZP+Cu, (C) Ce-TZP+Mn

coefficient of the controlling species. But this should not be the case in ceria-zirconia materials where the stabilizer CeO_2 has the same stoichiometry as the host ZrO_2 matrix at least up to very high temperature when it is reduced to Ce^{3+} introducing oxygen vacancies to balance its lower oxidation state. In this case the dopants become relevant in introducing lattice defects and enhancing cation diffusion through oxygen vacancies formation.

Fig. 5 TEM picture of Ce-TZP+Cu material showing a glassy phase pocket at the triple point

Fig. 6 Ce-TZP+Mn picture showing twins formed during the TEM analysis

From this point of view, two Cu^{+1} ions introduced three double charged oxygen vacancies whereas one Mn^{+2} or two Mn^{+3} ions form one vacancy only. Both can modify the lattice defect structure and the diffusion coefficient of the rate controlling species, namely cerium and zirconium cations[6,7]. These differences might depend upon the different dopant's ionic radii, as well as charges; in fact, in ceramics, the interaction between solutes and grain boundaries originates from (I) the electrostatic force between the charged ions and the electrical double layers in the grain boundary region and (II) the stress due to the ionic size misfit between the solute and the matrix ions. The theory most often used to explain the effect of a solute on grain-boundary motion is the Cahn solute drag model[8], which is based on solute segregation to or away from the grain boundaries, In this theory the drag force on grain boundary motion is due to an interaction energy between grain boundaries and solutes. When grain boundaries migrate, solute tend to follow the moving grain boundaries, since solutes are usually less mobile than grain boundaries, the grain boundary velocity is decreased by the solute drag force; Cu^{+1} is larger than either Mn^{+3} or Mn^{+2} and, therefore, one would expect Cu^{+1} to be a stronger segregant and perhaps a more effective grain-growth inhibitor. This simple solute segregation argument is, therefore, deficient. Therefore taking into account that in zirconia, densification is achieved by lattice diffusion ($\mathcal{D}_l$) and coarsening by surface diffusion mechanism ($\mathcal{D}_s$) it can be concluded that both CuO and MnO_2 affected the ratio ($\mathcal{D}_l/\mathcal{D}_s$) but with different effectiveness.

The reason why CuO improves the sintering rate more than MnO_2 does, seems to rely upon the defects forming ability of the Cu^{+1} species more effective than Mn^{+2} besides the fact that Cu^{+1} and Ce^{+4} ionic radii are very close both contributing by the same extent to the zirconia lattice distorsion, thus raising the sintering activity and at the same time weakening the retarding action of solid solution impurities on the grain boundaries movement[9,10].

On the other hand, being Mn^{+2} and Zr^{+4} ionic radii quite similar, practically neither the distorsion is expected by the manganese ion lattice diffusion nor the stabilization of the tetragonal form can be enhanced by its addition. In fact this evidence is reflected by the mechanical properties and the materials microstructure.

The mechanical properties obtained with samples sintered at 1530 °C for 4 hours are reported in Table I. The addition of both Cu and Mn increased the hardness due to the resulting microstructure with smaller grain size. SEM observations of the surface of fractured samples showed that at room temperature doped samples were fractured mainly along the intergranular surfaces whereas in the Ce-TZP transgranular fracture was also observed. Although mechanical properties were enhanced and quite good for both doped materials, Mn appeared to be more effective than Cu in raising toughness but specially bending strength; the small difference in the average grain size, between the two doped materials, could not be responsible for the quite different mechanical properties, but a TEM analysis, Fig. 6, revealed that twins were often present in the Ce-TZP+Mn microstructure whereas they have seldom been found in the Ce-TZP+Cu materials, suggesting that the transformation toughening mechanism was more likely to occur in the former material probably due to an overstabilization of the tetragonal phase when Cu was used.

Materials	tetr. (%)	σ (MPa)	Hv (GPa)	K_{Ic} (MPa√m)
Ce-TZP.	84	150	6	8
Ce-TZP+CuO	100	350	8	11
Ce-TZP+MnO2	100	450	8	13

Table I Mechanical properties obtained after sintering at 1530 °C for 4 hours

Before any conclusion is drawn, there is one more evidence worth mentioning: the increasingly dark colour of the Cu and Mn doped materials, Fig. 7. It was previously reported that "as fired" dark coloured samples of the ceria-zirconia alloys were good conductors, through an electronic mechanism based on the presence of Ce^{3+} species, even at room temperature. However, after 300 °C in air, the samples oxidized becoming less conductive and of light colour[11].

It is therefore inferred that Cu and Mn with their variable oxidation states may contribute to maintain down to room temperature reduced Ce^{3+} specie in excess to the natural redox behaviour of the undoped material. This might be a further contribution of these additives which will be object of impedance spectroscopy investigations to find out the duration and reversibility of the phenomena.

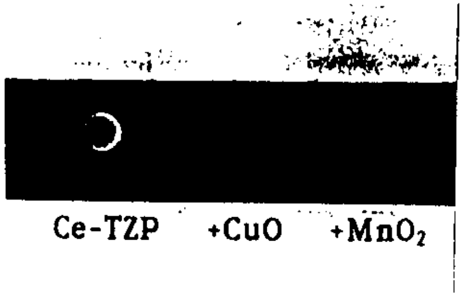

Fig. 7 Change of colour for the Cu and Mn doped materials due to the presence of Ce^{3+} specie

4. CONCLUSIONS

CuO and MnO_2 have shown to be good candidates as additives for the pressureless sintering of Ce-stabilized zirconia

High density, small grain size as well as almost fully tetragonal material could be achieved using short sintering time at a reasonable temperature.

The temperature at which the shrinkage begun did not decrease using MnO_2 or CuO, but at the same temperature the sintering rate was higher; MnO_2 and CuO were also very effective in improving mechanical properties (hardness, bending strength and toughness)

REFERENCES

1. R.L.K. Matsumoto - "*Aging behavior of Ce-stabilized tetragonal zirconia polycrystals*" J. Amer. Ceram. Soc. 71(3) C 128-C 129 (1978)
2. K. Tsukuma, M. Shimada - "*Strength, fracture toughness and Vickers hardness of CeO-stabilized tetragonal ZrO_2 polycrystals* " J. Mater. Sci. 20, 1178, (1985)
3. S. Meriani - "*A new single-phase tetragonal CeO_2-ZrO_2 solid solution*" Mater. Sci. and Engineering 71, 369, (1985)
4. F.F. Lange, M.M. Hirlinger - "*Hyndrance of grain growth of Al_2O_3 by ZrO_2 inclusions*" J. Amer. Ceram. Soc. 67(3)164-68 (1984)
5. R.C. Garvie, P.S. Nicholson - "*Phase analysis in zirconia systems*" J. Amer. Ceram. Soc. 55(6) 303-5 (1972)
6. R.J. Brook - "*Preparation and electrical behavior of zirconia ceramics*" In Science and technology of zirconia. Ed. by H.H. Heuer, L.W. Hobbs; Amer. Ceram. Soc. Publ., Columbus, Ohio, 1981, pp.272
7. S. Wu, R.J. Brook - "*Sintering additives for zirconia ceramics*" Trans. J. Ceram. Soc., 82, 200-205, 1983
8. H.M. Cahn - "*Impurity drag effect on grain boundary motion*", Acta Metall 10(9) 789-798 (1962)
9. M.M. Gadalla, J. White - Trans. Brit. Ceram. Soc., 65(7) 387 (1966)
10 Y. Dongseng - "*The microstructure of ceramics*", J. Chinese Ceram. 10(1), 25, (1982)
11. G. Chiodelli, A. Magistris, E. Lucchini, S. Meriani - "*Microstructure-electrical properties relations in sintered ceria-zirconia*" In Science of ceramics, vol.14 Ed. by D. Taylor, The Institute of Ceramics Publ., Stoke of Trent, U.K., 1988, pp.903-908