THE INFLUENCE OF THE ELABORATION'S CONDITIONS ON THE MICROSTRUCTURE OF A CERAMIC MATERIAL OBTAINED BY FREEZE-DRYING

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Abstract: *Freeze-drying is a dehydration proceeding of the products in a frozen state, which is based on the ice sublimation process. It is a method, which leads to a very good homogeneity of the products, and it allows obtaining very fine powders, which directs to reducing the sintering temperature. The microstructure was characterized by SEM. The microstructure of these polycristals is clean, homogeneous with lens-shaped glassy pockets at triple-points and there is no evidence for continuous films.*

Keywords: elaboration, ceramic material, microstructure, freeze-drying

FREEZE-DRYING PRINCIPLE

Freeze-drying is a dehydration proceeding of the products in a frozen state, which is based on the ice sublimation process. It is a method, which leads to a very good homogeneity of the products, and it allows obtaining very fine powders, which directs to reducing the sintering temperature. Freeze-drying always supposes three stages: freezing, sublimation and absorption of the residual water.

ELABORATION OF SAMPLES OF $ZrO_{2\ 0.91}\ Y_2O_{3\ 0.09}$

Elaboration of samples of $ZrO_{2\ 0.91}Y_2O_{3\ 0.09}$ was realized as follows:
a) *solution preparation*. It was used: $Zr(SO_4)_2\ 4H_2O$; $Y_2(SO_4)_3\ nH_2O$; solvent: H2O
b) *solution spraying*: the solution was sprayed into small droplets in liquid nitrogen.
c) *freeze-drying process*;
d) *calcinations of the freeze-dried powder – sulfate decomposition*;
e) *powder compacting* (isostatically compacting under a 4000 bars pressure);
f) *sintering* at four different temperatures.
T_f=1350, 1400, 1500, 1600 °C for t=5 hours, respectively T_f=1600 °C for t=40 hours.
The objective of these different thermic treatments is to create different microstructures.

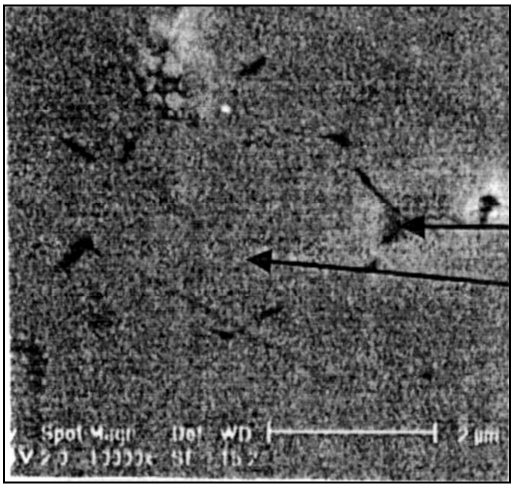
SAMPLES CHARACTERIZATION

The previous described five thermic treatments led to obtaining different structures with different densities.

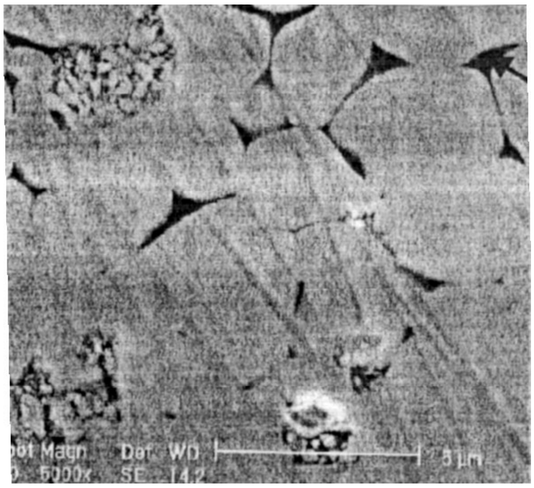
Sintering temperature	1350°C 5h	1400 °C 5h	1500 °C 5h	1600°C 5h	1600°C 40h
Sample density [g/cm^3]	5.12	5.18	5.22	5.41	5.61
[%] of theoretic density	86	87	88	91	94

As we can see from the described data, the rise of the sintering temperature as well as of the maintaining period at this temperature lead to the rise of the obtained ceramic material density, which is very important for the material practical applications.

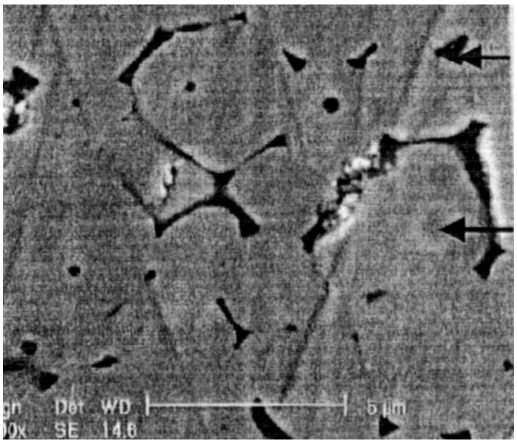
There were done also microscopic observations on the studied samples which followed two aspects: determining the grain size of the ceramic material, and also controlling the sample homogeneity, by analyzing the distribution of different impurities in different parts of the material. In fig. 1, we present the obtained micrographs for some samples of YSZ.



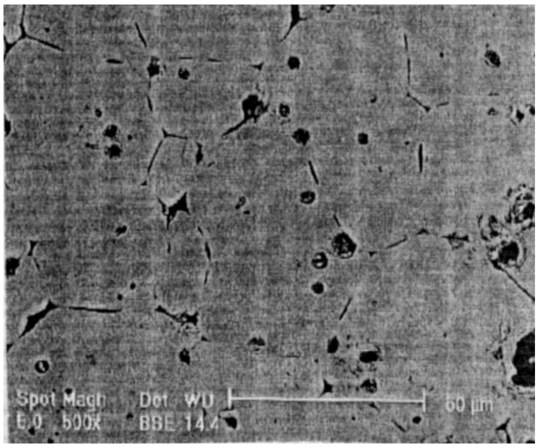
Sample sintered at 1400 °C for 5h



Sample sintered at 1500 °C for 5h



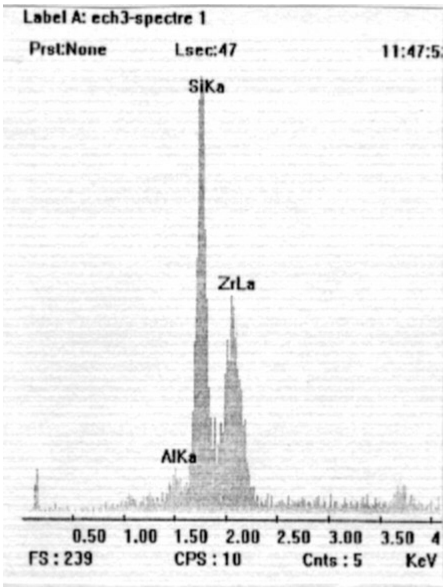
Sample sintered at 1600 °C for 5h



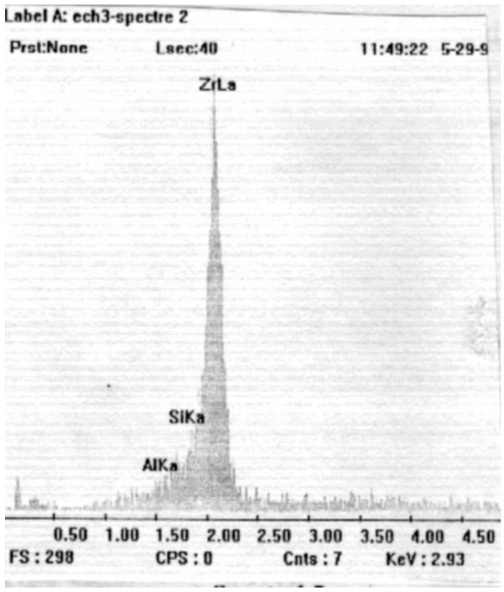
Sample sintered at 1600 °C for 40h

Fig. 1

One can observe out of the photographs that the sintering temperature significantly influences the grain size (the sintering temperature rise leads to a rise of the grain size from $\Phi g = 0.5\mu m$ for Tf = 1350°C to $\Phi g = 5\mu m$ for Tf = 1600°C). The maintaining period at the sintering temperature also influences the grain size (the maintaining period rise leads to a rise of the grain size from $\Phi g = 5\mu m$ for Tf = 1600°C for 5 hours to $\Phi g = 40\mu m$ for Tf = 1600°C for a period of time of 40 hours).
In order to control the homogeneity of the samples, polymerized samples were used which were not chemically treated. In table 2, the results of these analyses are presented for a sample (its conclusions being valid also for the others). As it results from the presented spectra, the chemical composition differs between the “interior” of the grain and its boundary. As a difference, the “interior” of the grain which from a chemical point of view has a “clean” aspect (there was no impurity detected), and at the grain boundary we can see the presence of the impurities, especially the silicon (which may come from the water used as a solvent to prepare the solution of sulfates).

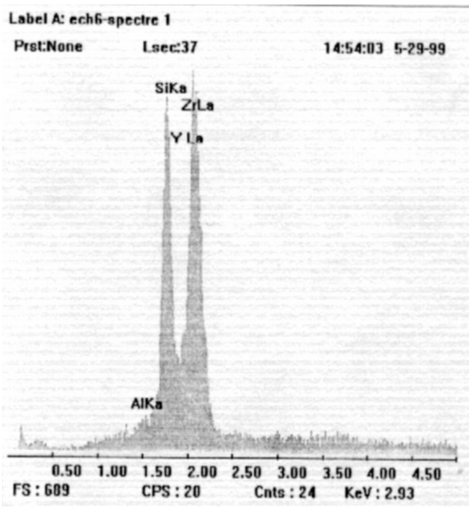


Spectrum 1

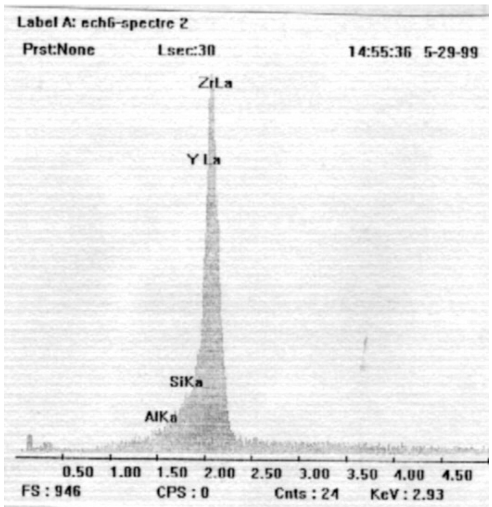


Spectrum 2

Sample sintered at 1500°C for 5h



Spectrum 1

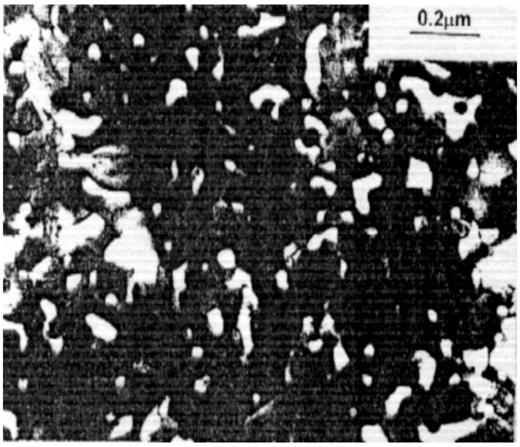


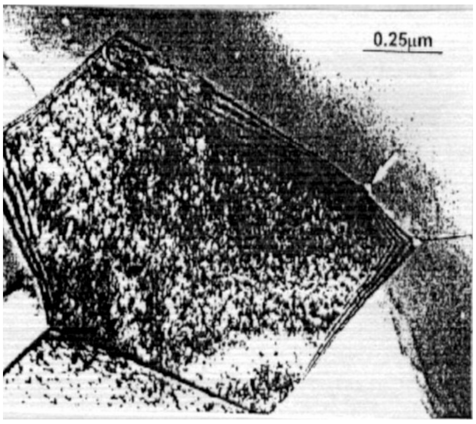
Spectrum 2

Sample sintered at 1600°C for 5h

Fig. 2 Distribution of impurities for samples of YSZ obtained of a freeze-dried powder
Spectrum 1 – realized at the grain boundary; Spectrum 2 – realized in the grain interior (bulk)

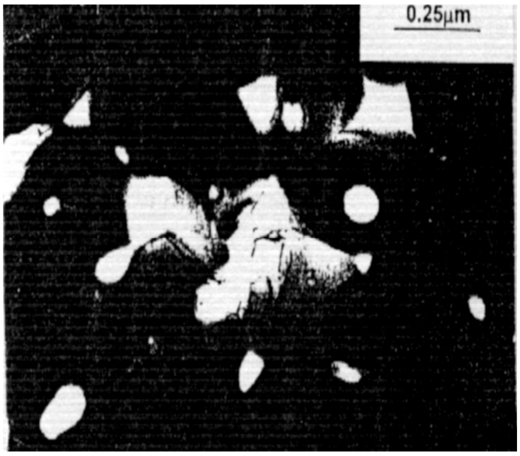
Another interesting aspect is the fact that as long as the sintering temperature and the maintaining period at this temperature grows, the boundaries of the grain become “cleaner”, a phenomenon of absorption of the glass phase taking place (silicon or its compounds) to the triple points (table 3 d) and also a concentration of the glass phase in the bigger “pockets” (table 3 c).

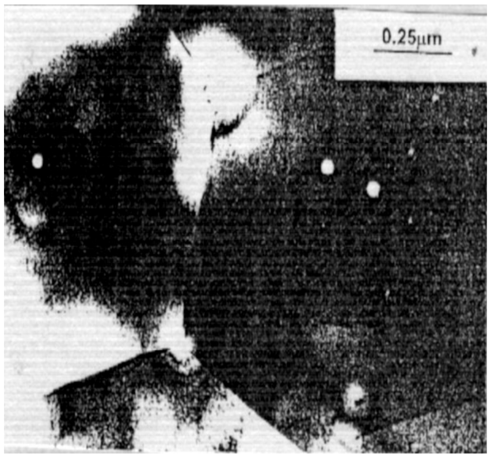




a) Distribution of glass pockets in the sample sintered at 1350 °C for 5 h

b) Triple points are lens in the sample sintered at 1350°C for 5 h





c) Distribution of glass pockets in the sample sintered at 1600 °C for 5 h

d) Triple points are lens in the sample sintered at 1600°C for 40 h

Fig. 3

If the sintering temperature and the maintaining period influenced the density as well as the microstructure, we cannot say the same thing about the micro hardness.

Sintering temperature	1350 °C 5h	1400 °C 5h	1500 °C 5h	1600 °C 5h	1600 °C 40h
HRC Hardness	69	70	71	72	72

Another interesting aspect is the presence of the cracks in the neighborhood of the print let by the penetrometer head. This can be explained by the chemical composition of the samples (YSZ is a ceramic material not very resistant to mechanical shocks).

CONCLUSION

The current work presents the influence of the process of producing the ceramics powder as well as the influence of the sintering temperature upon the micro-structure of the ceramics under study. Thus it was noticed that the sintering temperature plays a very important role both in determining the size of the grain (increasing the sintering temperature and the period of time this temperature is maintained for, all these lead to an important growing in size of the grain) and in the chemical structure of the limit of the grain, these influencing both the mechanic and the electric products made of YSZ.

Clear indications were found that glass distribution is a sensitive function of heat treatment and cooling rate. Our TEM observations also support these findings.

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