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Developing porous ceramics on the base of zirconia oxide with thin and permeable pores by crystallization of organic additive method

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Abstract. In this paper porous ceramics on the base of ZrO_2 nanopowders and micropowders has been developed by freeze-casting method. A zirconia/carbamide slurry was frozen in mold and dehydrated in $CaCl_2$ at room temperature. This simple process enabled the formation of porous ceramics with highly aligned pores as a replica of the carbamide crystals. The samples showed higher porosity of 47.9%. In addition, these materials could be used as membrane for air cleaning.

1. Introduction

Porous ceramics is widely used since 1950's and has a wide range of application in different fields now [1, 2]. Ceramics on the base of refractory oxides in particular ceramics on the base of ZrO_2 has a greatest demand. Zirconium dioxide ceramics has good physical and chemical properties (strength, chemical resistance, crack resistance and etc.). Zirconium dioxide ceramics can be used as membranes for air cleaning from dangerous for organism particles (less 5μm).

There are a lot of methods for obtaining porous ceramics but significant disadvantage of these methods is impossibility to control pores morphology. Application of organic additives crystallization in suspension because of change of temperature method can be used to solve this problem [3, 4]. This method allows to regulate pores morphology in the sample and does not pollute sample by impurities from burnable additives.

The aim of this research is to develop method for obtaining porous ceramics based on ZrO_2 powders of various dimensions with application of organic pore agent.

2. Experimental Part

Zirconium dioxide powder of micron size (0.23 μm average particle size, produced by the Chepetsk Mechanical Factory, Russia) and nanopowder (30 nm average particle size, produced by the Seversk Chemical Factory, Russia) were used to obtain porous ceramics. Specific surface area of powders was determined by Surface Area and Pore Size Analyzer Quantachrome Nova-2200-e. Powders were mixed with mass ratio 50:50 in ball mill with zirconia mill and balls. Samples from 100% micronpowder and nanopowder were produced for comparison. Morphology and structure of powders were studied using analytical Field Emission SEM JEOL JSM-7500FA.

Suspension of carbamide prepared by dissolved of carbamide granules in hot water (t=80 ^{0}C) with mass ratio 2:1 (carbamide: water) was used to obtain porous ceramics. The prospect of the use of

carbamide is the ability to produce aligned crystals (in the form of needles) of carbamide during crystallization. Behavior of the carbamide crystals during heating was analyzed using thermal analyzer NETZSCH STA 449 F3 Jupiter®. Samples were formed by casting method in conditions dramatic change temperature. Figure 1 demonstrates the process scheme. Complex mold has been developed for crystallization process and instantaneous temperature change at the bottom of the form (to form elongated in one direction, crystals). The bottom of the mold was made from metal (thermal conductivity is 197 W/(m^0C), walls of the mold were made from polyurethane (thermal conductivity is 0.315 W/(m^0C) In this mold instantaneous change of slurry temperature was achieved only on its bottom by combination of materials with different thermal conductivity. Walls and the top part of the mold were isolated from the external environment by a thin film to achieve gradual cooling of the slurry from bottom to walls of the mold. Drying of the samples was made in desiccator over calcium chloride granules to remove excess water. Samples were heat treated at 1580°C in air, rate of temperature rise ~ 2°C per a minute, curing at finishing temperature for 2 hours.

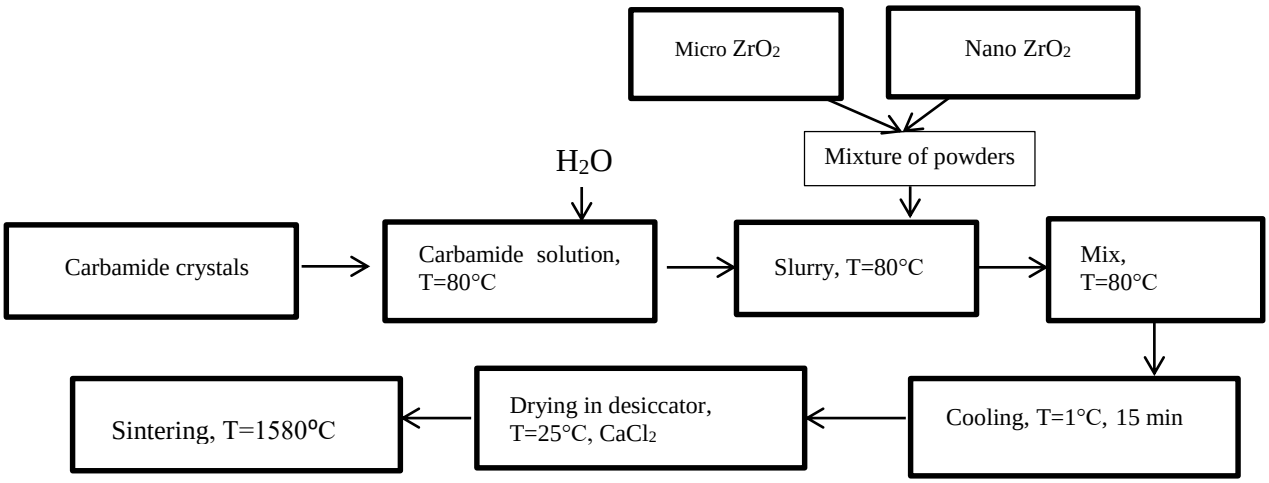


Figure 1. Scheme of porous ceramics obtaining by crystallization method of burning addition

3. Results and Discussion

Differential scanning calorimetry (DSC) and thermogravimetry of needle carbamid crystals were carried out to research the process proceed in samples at carbamide crystals heating (figure 2). Type of DSC graph demonstrates that complex endothermal reaction is carried out at heating. Two steps fixe on mass loss curve. The first stage is characterized by greater weight loss (49.06%) than the second stage (44.58%). The first weight loss occurs at the temperatures ranging from 130 to 256^{0}C due to the fact that melt of carbamide is carried out at the heating from 130 ^{0}C to 150^{0}C, biuret ($C_2H_5N_3O_2$ or $(H_2NCO)_2NH$) forms from 232^{0}C to 256^{0}C under simultaneous production of ammonia.

$$2H_2NCONH_2 \longrightarrow (H_2NCO)_2NH+NH_3$$

The second loss of weight at the full decomposition of carbamide is due to rejection of isocyanic acid (HNCO) in the temperature range from 365 to 405 ^{0}C. The cuts of samples before firing were made to investigate carbamide crystals obtaining in samples.

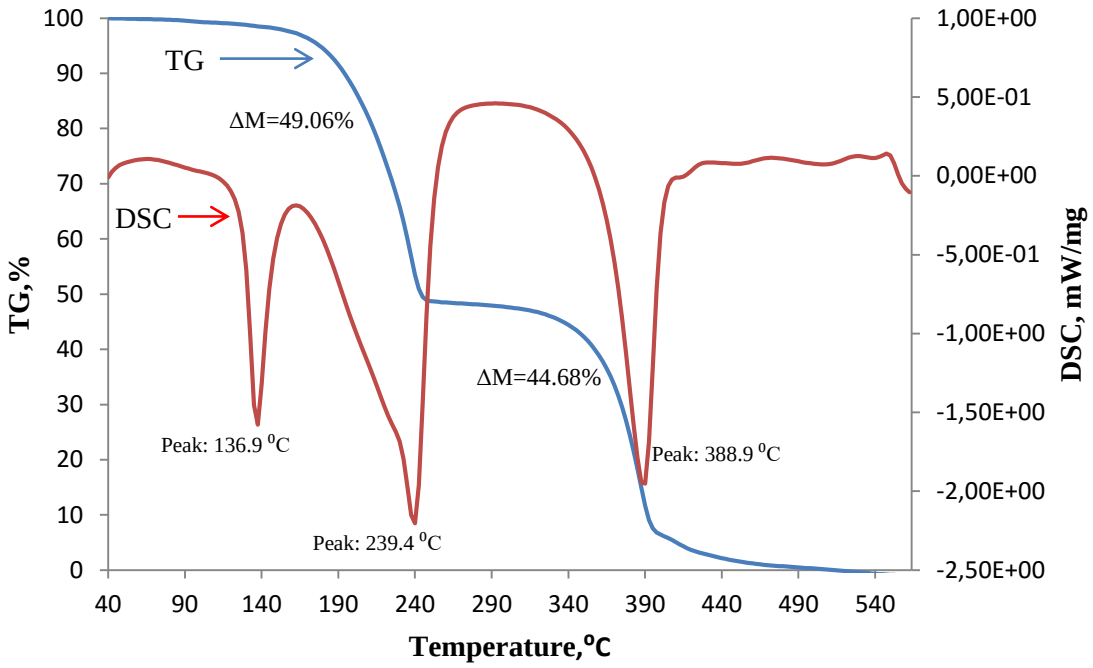


Figure 2. Differential scanning calorimetry and thermogravimetry of needle carbamide crystals

Figure 3 demonstrates carbamide crystallization in form of thin needles in sample volume. In this case particles of oxide powders surround each crystal. Carbamide crystals are burned in firing process with pores forming. Sintered samples have permeable pores in form of needles. Type of porosity is clearly visible on side section and top surface of sample (figure 3).

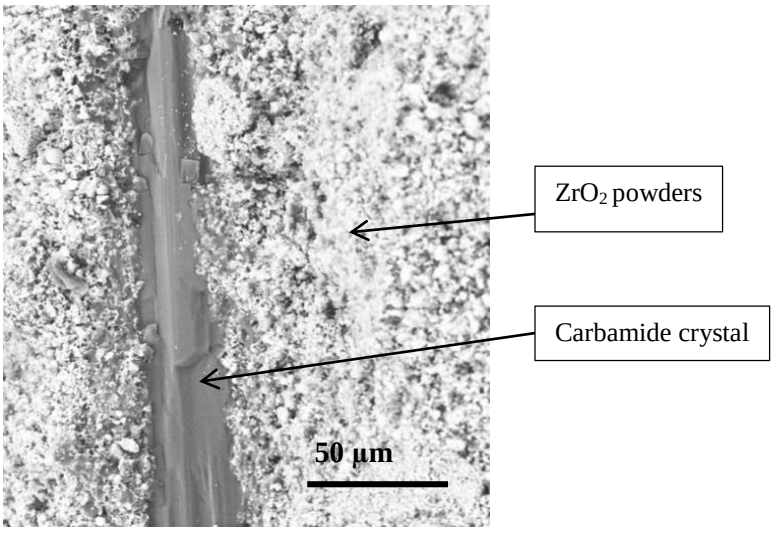
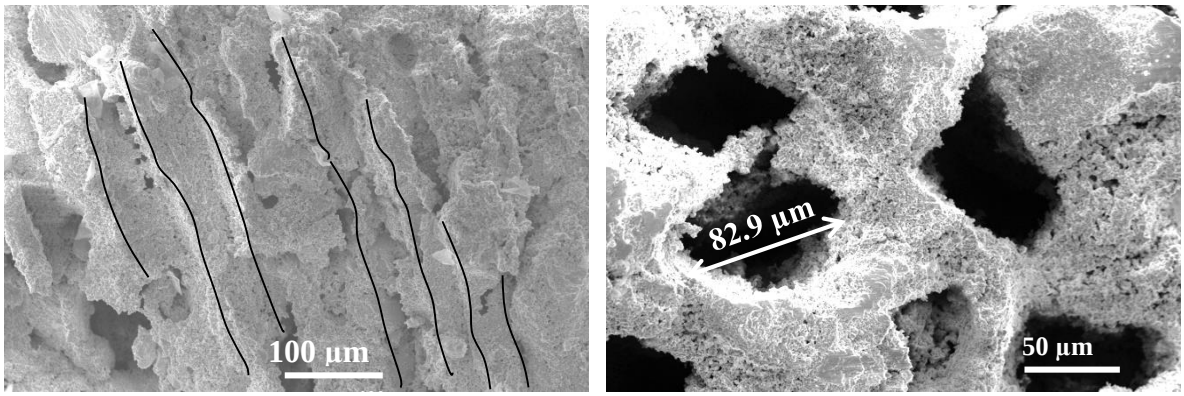


Figure 3. Photo of raw samples consist of 50 mas.% nanopowder ZrO_2 and 50 mas.% micron powder ZrO_2

Pores formed after removing carbamide crystals have an aligned form (figure 4a). Length of channels achieves 5 mm, pores width changes from 0.2 to 200 µm (figure 4b).



a b

Figure 4. Photo of sintering samples consist of 50 mas. % nanopowder ZrO_2 and 50 mas. % micron powder ZrO_2 (a-side elevation, b- plan view)

4. Conclusion

Application of organic additives crystallization in slurry method allows to obtain ceramics with thin permeable pores and total porosity 48%. Ceramics can be prepared with a predetermined level and morphology of pores by varying the powder composition, the slurry temperature, the amount of carbamide in solution and the mold. Samples obtained in the experiment have pores from 0.2 to 200µm size, that allows to use this type of ceramics for gas purification from large and small particles (until 0.5 µm).

References

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