KINETICS OF NANOCRYSTALLINE PHASE TRANSFORMATIONS IN SPRAY PYROLYSED ZnO PARTICLES

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Abstract

The thermal behavior of ZnO powder obtained by ultrasonic spray pyrolysis of nitrate solution ($c=0.8mol/dm^3$, $D_0=2.695\mu m$, $T_{max}=600^0C$, $F_G=1.2dm^3/min$) was investigated using non-isothermal differential scanning calorimetry (DSC, heating rates 5, 10, 15, $20^O/min$). The exothermic heat effects at the temperature range from 350 to 500^0C were linked to particles structural data obtained by XRD, SEM and TEM analysis. Produced particles are characterized by uniform submicronic size ($D=800nm$, $BET=4.94m^2/g$), high phase purity and granular or circular "open" surface due to the presence of primary crystallites ($d= 20nm$). Observed structural changes during heating of this powder were attributed to simultaneous processes of nucleation and growth of primary crystallites inside the produced particles.

1. Introduction

Nanocrystalline state of material is currently receiving much attention due to virtue

of special physical, chemical and mechanical properties that make them suited for different usage [1]. Strong research efforts have been devoted to understanding the basic properties of this metastable structure and transformations that should be expected during such powders processing (relaxation, equilibration of concentration, precipitation, nucleation, crystal growth, etc.). Those processes must be known if conducted growth of specific particles morphology, as well as required fraction crystallized is wanted to be attained.

Zinc oxide, due to its wide range of applications, especially in electronics, energy conversion systems and catalysts has been intensively studied for many years. Today, in the nanocrystalline form composed from crystallites with dimension ranging from several to tens of nanometers, thanks to some new properties, zinc oxide powder is in the focus of research interest again[2].

Compared to the other processing methods, spray pyrolysis process enables synthesis of ultra fine powders and thin films synthesis with controllable particle properties [2]. In our previous papers [4,5] it was shown how the particle size and morphology can be affected by different processing parameters during synthesis of oxide powders by this process. It was shown that conduced evaporation, drying, precipitation and decomposition of droplets during thermolysis leads to the spherical, solid, agglomerate-free, submicronic or nanosized particle synthesis with desired chemical and phase content.

The results of the comparative investigations of thermal behavior during linear heating of ZnO nanocrystalline powder produced by ultrasonic spray pyrolysis and observed structural changes in particles were reported in this paper.

2. Experimental

The aerosol was made ultrasonically (mist generator 1.7 MHz) from the 0.8 mol/dm^3 Zn(NO$_3$)$_2$·6H$_2$O precursor solution. The aerosol average droplet size and the mean particle size were estimated from the precursor properties (pH=3.9, ρ=1.1047 g/cm^3, μ=0.5302 mPas and σ=67.4mN/m) in accordance to the previously proposed procedure [5] to be 2.695 μm and 619 nm, respectively. Aerosol was introduced in a horizontal twin-zone tubular flow reactor with air as a carrier gas (flow rate 1.2 dm^3/min). Decomposition profile was follows: 200^{0}C in the first, and 600^{0}C in the second reaction zone. The droplet/particle residence time and velocity were 5s and 0.252 m/s, respectively. The aerosol droplet number density was maintained at N$_0$=1.53·10^5 droplet/cm^3 in order to avoid the droplet coalescence.

Differential scanning calorimetry (DSC) measurements were conducted using a Shimadzu DSC-50 on the 8 mg powder sample, placed in platinum open sample pans

and nitrogen atmosphere. The instrument was previously calibrated with In, Sn and Zn standards. Non-isothermal DSC curves were obtained in the range of 25-600°C at heating rates 5, 10, 15 and 20°C/min. Each sample, after cooling to room temperature was run by the same heating procedure according to obtain the baselines.

Compositional homogeneity and particle morphology of as-prepared powder were determined in accordance to scanning electron microscopy (SEM, JEOL-JSM-5300) and energy dispersive spectroscopy (EDS, QX-2000). Inner particle structure was examined by transmission electron microscopy (TEM, JEOL-100CX), while BET (Micromeritics) was used for the determination of particle surface characteristics.

Crystal phases of as-prepared and thermally treated (after DSC measurements) ZnO powder samples were revealed by X-ray powder diffraction using a Philips PW 1710 Automated Powder Diffraction with CuKα radiation. Measurements were done with scanning step width of 0.02 and time of 2s, while program FULLPROF was used for data analysis.

3. Results and Discussion

The SEM microphotograph (Fig.1-left) shows the typical structure of as-prepared ZnO powder. The obtained particles are slightly agglomerated and exhibit spherical morphology. Each particle represents the aggregate of smaller grains, integrated in open circular or grape cluster structure. Loosely sintered particles evident inside agglomerates of spherical or rod-like grains, indicates that the powder obtained using spray pyrolysis method is highly reactive. Statistical review of obtained SEM microphotographs implies uniformity of particle size and shapes with the mean particle size of 800nm. BET specific particle surface is determined to be 4.94 m^2/g. Assuming this value, equivalent particle diameter is calculated to be 216nm. Discrepancy between calculated and obtained values indicates that formed particle is not fully dense. TEM inner structure (bright field on Fig.1-right) proved nanoporosity. It is noticeable that particles are composed from smaller unities of primary subgrains, sized around 20nm, as well as small quantity of amorphous material. XRD phase analysis detects zinc oxide formation in as-prepared powder (JCPDS card 36-1451), but also indicated nitrate hydroxide hydrate phase (JCPDS card 24-1460) presence, as a consequence of the precursor incomplete decomposition. DSC analysis of powder implies the loosing of the residual crystal water up to 200°C, while finishing of the decomposition of the nitrate hydroxide hydrate phase has occurred at the temperatures up to 350°C (Fig.2-left, inset). Low temperature structural transformation can be noticed on the same DSC curve in the temperature range from 380 to 500°C.

In order to obtain the kinetic description of structural transformations that take place during additional heating of as-prepared ZnO nanocrystalline powder, a series
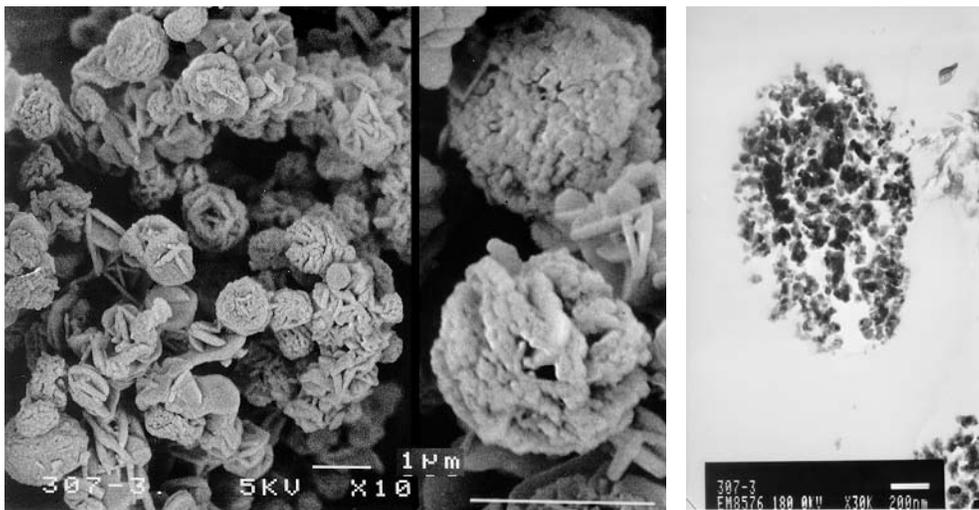
Fig 1. SEM micrograph and TEM inner structure of as-prepared ZnO particles

of DSC measurements with different heating rates (5, 10, 15 and 20^{0}C/min) were performed according to the theory [6-8]. Observed exothermic effects (Fig.2-up) imply the irreversible structural changing processes presumably associate with overlapping of quasi nucleation and growth of nanocrystallites followed by heat releasing [9]. Only in the case of the heating rate of 20°C/min two separate peaks could be observed.

Due to the fact that primary crystallite size in the as-prepared powder is nanosized, as well as that formed nucleation sites are present randomly in the particle together with the small quantity of amorphous phase (Fig.1-right), structural changes taken place during powder heating should be observed by XRD structural analysis.

Broadening of the diffraction lines is noticeable for all powder samples (Fig.2-down). Calculated value of crystallite size in as-prepared powders (23.6nm) is in good agreement with crystallite size observed from TEM microphotograph. Average crystallite size (nm) and residual microstrains (‰) in powders after heating are presented in Tab.1. Obtained results imply slight increase of crystallinity with increasing of the heating rate, but average crystallite size does not change signifi-

cantly. Only in the case of the heating rate of 20°C/min was noticed the deflexion in crystallite size, because this heating rate stimulate not simplify crystal growth but arising microstrains.
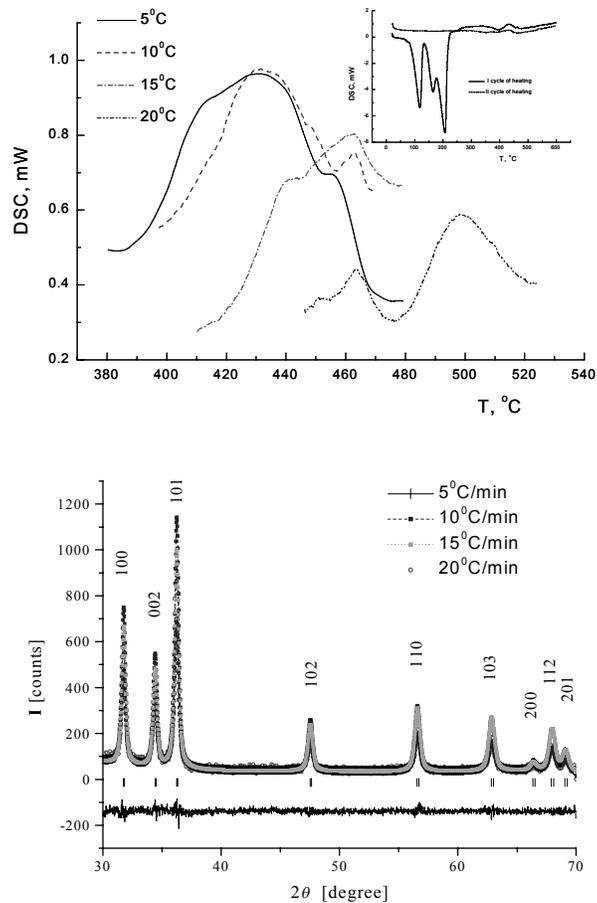

Fig.2. Structural transformations during linear heating of as-prepared ZnO powder and inset of the DSC curve - heating rate of 100C/min (up) and XRD structural analysis of thermally treated powders (down)

The crystallization kinetics based on these data is usually interpreted in terms of the Johnson-Mehl-Avrami (JMA) equation extended for non-isothermal conditions. The validity of such nucleation-growth model is based on the assumptions that entire nucleation process takes place during the early stages of the transformation and

becomes negligible afterward[6,7]. Also, a new crystalline phase have to grow from a constant number of nuclei and all nucleation must be completed before the macroscopic crystal growth started. In that case, the crystallization rate is defined only by temperature and does not depend on the previous thermal history.

For nanocrystalline ZnO particles observed structural transformation is dependent on the rate of temperature change. Specific heat flow normalized per sample mass (ϕ) and the crystallization enthalpy (ΔH_c) are easily obtained by integration of DSC curves presented on Fig.2-left. Decreasing trend of ΔH_c with increasing of the heating rate was found (Tab.1). Obtained values reveal that nucleation-crystallization process has complex nature, probably due to an overlapping of these processes at the beginning of the transformation. Only in the case of the heating rate is 20°C/min, the nucleation and crystal growth peaks are separated by a temperature gap. With increasing of the heating rate the number of nuclei decreases, which corresponds to a smaller nucleation time. Another possible explanation is that the measured data corresponds to the more-complex process, such as the secondary nucleation induced by crystal growth or change in intercrystalline volume fraction due to crystallite-growth. In order to estimate the intercrystalline enthalpy we used procedure proposed by Wang [9]. The obtained values presented in Tab.1, indicate existence of the large amounts of intercrystalline components in samples.

Table 1. Structural and kinetic parameters in ZnO powders after linear heating (based on XRD and DSC analysis)

sample	heating rate 5°C/min	heating rate 10°C/min	heating rate 15°C/min	heating rate 20°C/min
Crystall. size, nm	26.7	27.2	29.5	27.7
Microstrains, ‰	25	23.5	27.8	35.6
ΔH_C, J/g	29.9	26.6	4,6	1.8
ΔH_{IC}, kJ/mol	178.3	138.9	16	1.7
α	0.62	0.54	0.55	5.8
E_a, kJ/mol	190.7	226.3	70.2	570.4

Under the restrictions outlined above the application of the JMA model considers the 0.632 as a value for the fractional conversion α in the DSC peak maximum. According to obtained experimental data calculated α values at performed heating rates are somewhat lower (Tab.1). Because of that, double logarithmic plot ln[-ln(1-α)] as a function of reciprocal temperature is shown on Fig.3-up. The slope of this
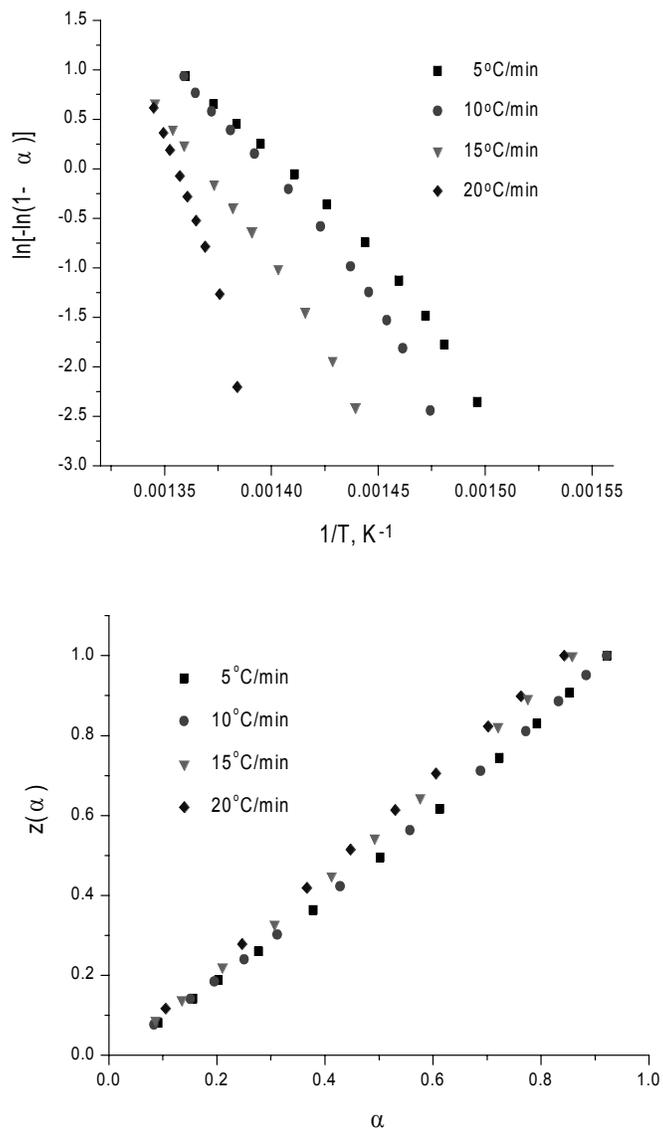
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Fig. 3. The double ln plot obtained from DSC data (up) and normalized
   z(α) values (down)

plot is expressed in terms of activation energy (E_a) and kinetic exponent (m). Presented values (Tab.1) should be plotted linearly in the case that the JMA model is fulfilled, but it has been shown that linear function could be obtained even in the case that JMA model is not valid[7].

A more reliable test is based on the properties of the $y(\alpha)$ and $z(\alpha)$ functions obtained by transformation of DSC data [8]. These functions are defined for non-isothermal conditions as follows: $y(\alpha)=\phi\exp(-E_a/RT)$ and $z(\alpha)=\phi T^2$. The normalized values of $z(\alpha)$ (within the 0-1 range) as a function of fractional conversion α are presented on Fig.3-down. The similar feature (the same deviation from convex function) is also obtained for $y(\alpha)$ implying that transformation behavior of observed exothermal effects cannot be modeled by JMA nucleation-growth equation.

4. Conclusion

In the light of these facts, it can be concluded that nature of the observed structural changes during heating of nanocrystaline ZnO powders obtained by spray pyrolysis should be discussed from the point of integrated processes of nucleation and crystal growth of the residual amorphous phase, together with the pronounced influence of initially formed crystalline component relaxation.

The as-prepared particles exhibit rough surface morphology caused by the presence of subunits, smaller grains organized in cluster structure. The presence of primary crystallites having the average size around 20nm is proved by TEM and XRD structural analysis. Particle cluster structure comprising of both granular and rod-like subgrains, reveals low dimensionality crystalline growth from numerous nucleation sites mainly formed at the particle surface during spray pyrolysis process. Complexity of the nucleation and growth processes in the investigated samples becomes quite evident from the shape of the $y(\alpha)$ and $z(\alpha)$ function with implication that JMA model could not be used for the crystallization kinetic evaluation.

Acknowledgements

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