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The nature of structural changes in nanocrystalline ZnO powders under linear heating conditions

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Abstract

The nature of exothermal and irreversible structural changes observed during linear heating of nanocrystalline ZnO powders was investigated using differential scanning calorimetry, X-ray, SEM and TEM analysis. Nanocrystalline ZnO powders were obtained by ultrasonic spray pyrolysis of 0.8 mol/dm^3 zinc nitrate solution and subsequent decomposition of 2.7 μm sized droplets in the temperature range up to 600 °C, $F_{air} = 1.2$ dm^3/min. Produced particles are characterized by uniform and submicronic size, BET = 4.94 m^2/g, high phase purity and granular or circular "open" surface as the consequence of primary crystallites presence with average size of $d = 20$ nm. The observed quasi nucleation-growth process during heating of this powder was discussed in the terms of primary crystallites structural changes.

Keywords: Nanocystalline powders; Structural changes; Thermal properties; ZnO

1. Introduction

Zinc oxide, due to its wide range of applications, especially in electronics, optoelectronics, energy conversion systems and catalysts has been intensively studied for many years. Currently, a different form of nanocrystalline ZnO material composed from ultrafine crystallites with dimensions ranging from several to tens of nanometers, is receiving much attention due to some new and special properties.[1] Strong research efforts have been devoted to understanding its metastable structure and transformations that should be expected during powders processing. Those processes must be known if conducted growth of the specific particles morphology, as well as required fraction crystallized is wanted to be attained. Spray pyrolysis is one of the most promising techniques for the ultra fine powders and thin films production.[2] In our previous papers[3,4] it was shown how the particle size and morphology can be affected by changing the processing parameters during the spray pyrolysis process. It was shown that suitable control of droplet transformation during thermolysis (evaporation, drying, precipitation and decomposition) leads to the spherical, solid, agglomerate-free, submicronic or nanosized particle evolution with conducted 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 correlation of observed exothermal effects with structural changes in particles will be reported in this paper.

2. Experimental

The precursor was prepared by dissolving appropriate amounts of corresponding metal salt $Zn(NO_3)_2 6H_2O$ in distilled water in order to obtain a 0.8 mol/dm^3 solution. The solutions properties were as follows: pH: 3.9, density: 1.1047 g/cm^3, viscosity: 0.5302 mPas and surface tension: 67.4mN/m. The aerosol based on this solution was made ultrasonically (mist generator 1.7 MHz). The aerosol average droplet size and the mean particle size were estimated in accordance to the previously proposed procedure[4] as 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 °C in the first and 600 °C in the second reaction zone. The droplet/particle residence time and

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velocity were 5 s and 0.252 m/s, respectively. The aerosol droplet number density was maintained at $N_0 = 1.5310^5$ droplet/cm^3 in order to avoid droplet coalescence.

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.

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 the room temperature, was run by the same heating procedure in accordance to obtain the baselines.

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 CuK_α radiation. Measurements were done with scanning step width of 0.02 and time of 2 s, while program FULLPROF was used for data analysis.

3. Results and discussion

The SEM microphotograph of the as-prepared ZnO powder is presented at Fig. 1. The slightly agglomerated particles exhibit spherical morphology. Visible surface revealed rough and composite particle structure. 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, indicating that powder obtained through spray pyrolysis method is very reactive. Statistical review of obtained SEM microphotographs implies uniformity of particle size and shapes with the mean particle size of 800 nm. BET specific particle surface is determined to be 4.94 m^2/g. TEM inner structure (bright field on Fig. 1b) proved that obtained particles are composed from smaller unities of primary subgrains, sized around 20 nm, as well as a small quantity of amorphous material.

Structural analysis based on XRD data and expressed through primary crystallite size changes was done for as-prepared ZnO powder as well as for the samples after non-linear heating, Fig. 2. Phase determination proved the ZnO formation (JCPDS card 36-1451) in as-prepared powder, but a nitrate hydroxide hydrate phase (JCPDS card 24-1460) is also detected, due to incomplete decomposition. DSC analysis implies the loosing of residual crystal water up to 200 °C, while complete decomposition of a nitrate hydroxide hydrate phase was occurred at the temperatures up to 350 °C (Fig. 3, inset). Due to the fact that primary crystallite size in the as-prepared powder is nanosized peak broadening is evident. Calculated values of average crystallite size (nm), as well as residual microstrains (‰) are: 26.78 and 25 (5 °C/min); 27.2 and 23.5 (10 °C/min); 29.5 and 27.8 (15 °C/min); 27.7 and 35.6 (20 °C/min), respectively. The obtained results imply a slight increase of crystallinity with an increase of the heating rate, but average crystallite size does not change significantly.

In order to obtain the kinetic description of structural transformations that occur during additional heating of as-prepared ZnO nanocrystalline powder, a series of DSC measurements with different heating rates (5, 10, 15 and 20 °C/min) were performed according to the theory.[5–7] Exothermic effects in the temperature range from 380 to 500 °C (Fig. 3) imply the irreversible

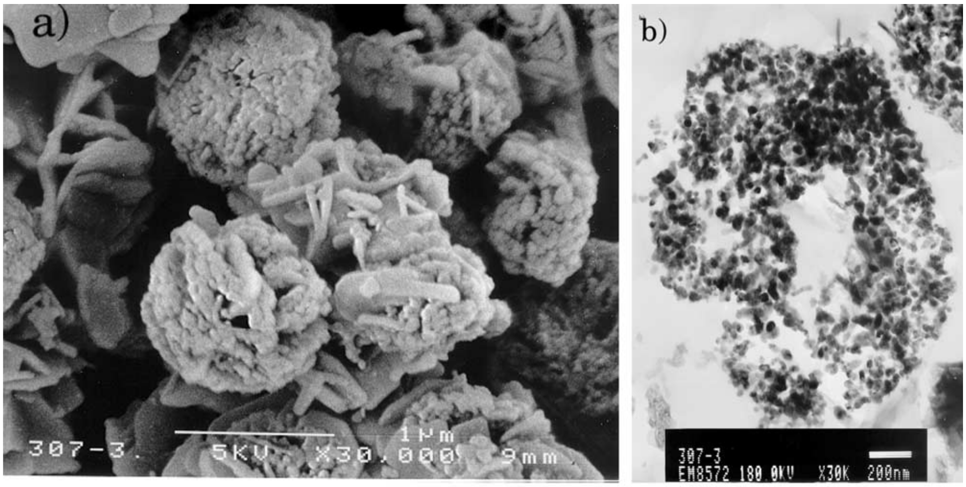

Fig. 1. SEM micrograph and TEM inner structure of as-prepared ZnO particles.

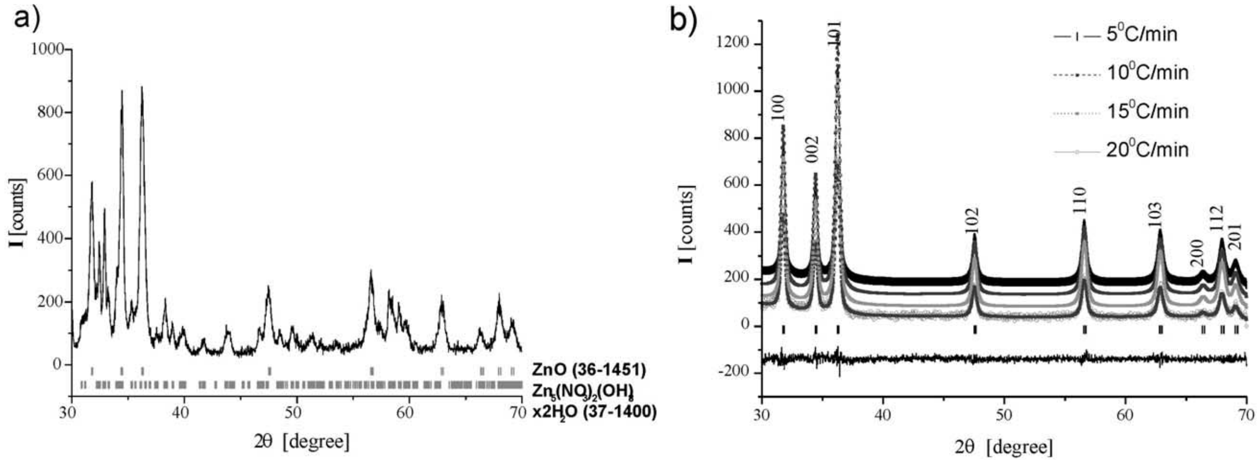

Fig. 2. XRD of as-prepared ZnO powders and structural analysis of thermally treated powders.

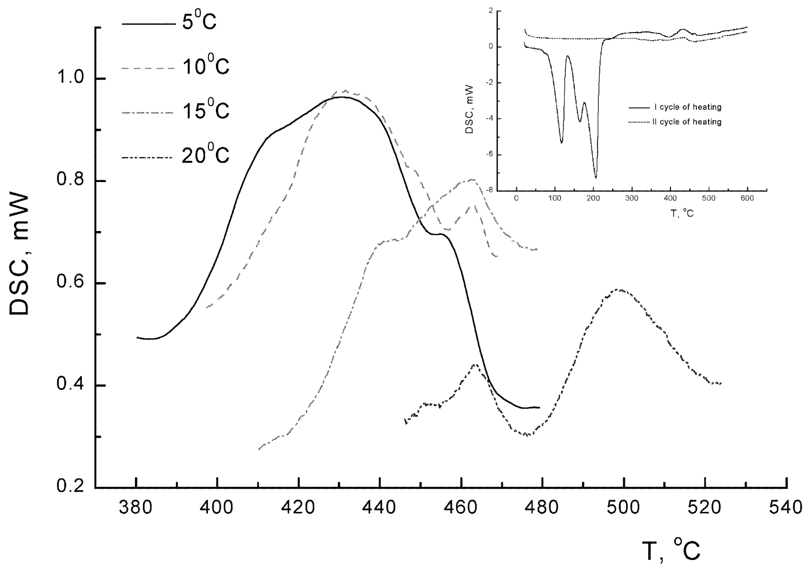

Fig. 3. Structural transformations during linear heating of as-prepared ZnO powder and inset of the DSC curve (heating rate of 10 °C/min).

structural changing processes presumably associate with quasi nucleation and grown of nanocrystallites followed by heat releasing.[8]

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 has 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, so can be associated to DSC linear heating.

In partially 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. 3. Decreasing trend of ΔH_c with increasing of the heating rate was found: 29.93 J/g—5 °C/min; 26.65 J/g—10 °C/min; 4.66 J/g—15 °C/min; 1.85 J/g—20 °C/min. 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 shorter nucleation time. Another possible explanation is that the measured

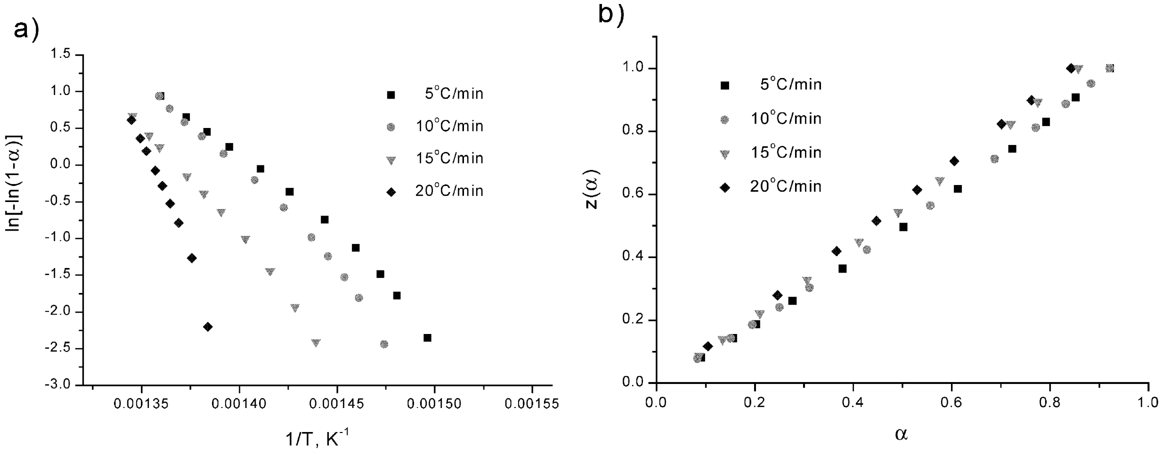

Fig. 4. The double ln plot obtained from DSC data and normalized z values.

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.[8] The obtained values: 178.3 kJ/mol—5 °C/min; 138.9 kJ/mol—10 °C/min; 16kJ/mol-15 °C/min; 1.7 kJ/mol—20 °C/min, indicate existence of large amounts of intercrystalline components in samples.

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 the obtained experimental data calculated α values at performed heating rates are somewhat lower. Because of that, double logarithmic plot $\ln[-\ln(1-\alpha)]$ as a function of reciprocal temperature is shown in Fig. 4a. The slope of this plot is expressed in terms of activation energy (E_a) and kinetic exponent (m). Presented values 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]

So, a more reliable test based on the properties of the $y(\alpha)$ and $z(\alpha)$ functions is performed. These functions are defined for non-isothermal conditions by combining basic kinetic equation and the generalized time introduced by Ozawa as follows[7]: $y(\alpha) = \phi\exp(-E_a/RT)$ and $z(\alpha) = \phi T^2$. Substituting reflects the nature of functions so they become invariable with respect to temperature heating rate, but quite sensitive to subtle changes in kinetic model. Assuming this, same deviation from convex function is obtained for both functions implying that transformation behavior of observed exothermal effects cannot be modeled by JMA nucleation-growth equation. Normalized values of $z(\alpha)$ (within the range 0–1) as a function of fractal conversion α are presented on Fig. 4b.

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

4. Conclusion

Nanocrystalline ZnO powder is synthesized by ultrasonic spray pyrolysis of 0.8 mol/dm^3 nitrate solution. The particles obtained exhibit rough surface morphology caused by the presence of subunits, smaller grains organized in cluster structure. Due to the short droplet/particle residence time in reaction zone, poor crystalline ZnO phase, as well as small quantity of residual amorphous phase is detected in the as-prepared powder together with inetrmediate species. The presence of primary crystallites having the average size around 20 nm is proved by TEM and XRD structural analysis. All this seems to be consistent with the complex nature of the transformation processes observed during powders non-isothermal heating. 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 the implication that JMA model could not be used for the crystallization kinetic evaluation.

Acknowledgements

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