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Preparation of nanostructured Zn–Cr–O spinel powders by ultrasonic spray pyrolysis

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Abstract

Ultrasonic spray pyrolysis (1.7 MHz) has been applied for the generation of zinc chromium oxide submicronic (470 nm) particles from the corresponding metal nitrate solution. Heterogeneous gas–liquid/solid chemical reactions occurred in dispersed systems (aerosols) at 1173 K with the residence time ranging from 3 to 6 s. Such a synthesis method enables a high surface reaction and stoichiometric retention at the droplet scale that is of special importance when functional materials with sensing properties are considered. Consequently, homogeneous distributions of the constituting elements and zinc to chromium atomic ratio of about 0.7 are proved by EMAX analysis. The particle morphology, revealed mostly as a composite structure, comprised of primary crystallites smaller than 70 nm. The particle crystalline structure, phase content and decomposition behavior were analyzed in accordance with various methods of analysis (X-ray powder diffraction (XRD). differential scanning calorimetry (DSC). differential thermal analysis (DTA), scanning electron microscopy with X-ray microanalyser (SEM–EMAX)) and discussed in terms of precursor chemistry and process parameters. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Electronic and structural ceramic components require good homogeneity both in composition and microstructure. The constituent powder processing method primarily affects high reliability as a main characteristic. Synthesis through aerosols enables generation of fine single as well as multicomponent powders with improved compositional homogeneity provided by a higher surface reaction in the absence of compositional segregation as a first step toward advanced ceramics applications.[1,2]

It is well established that some spinels have advanced gas sensing and catalytic properties.[3,4] A number of ceramic materials with a spinel crystal structure are used for humidity sensing.[5] Spinels, such as $ZnCr_2O_4$, are thermally stable and very suitable for aggressive environments with a long exposure time.[6] Stoichiometry and microstructure of ceramic chromates have the most important influence on their sensitivity and sensing properties.[4]

With respect to the above mentioned, the main goal of this work is to demonstrate ultrafine submicronic Zn–Cr–O powders synthesis by the spray pyrolysis method, as well as to establish the relations between structural homogeneity and morphology of powders and processing parameters.

2. Experimental

Aqueous solutions for atomization were prepared by dissolving appropriate amounts of corresponding metal salts $Zn(NO_3)_2{\cdot}6H_2O$ and $Cr(NO_3)_3{\cdot}9H_2O$ (Merck, p.a. 99,9%), in distilled water in order to obtain a 0.03 mol/dm^3 solution. Assuming that the precursor stoichiometry persisted in final particles, the cation ratio of Zn:Cr = 1:2 is chosen as the starting composition. Precursor characterization included measurement of density, pH, viscosity and surface tension and obtained values are 1.004 g/cm^3, 1.988, 0.4138 mPas and 67.85 mN/m,

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respectively. Aerosols based on these solutions were made ultrasonically (ultrasonic mist generator 1.7 MHz, with the aerosol mean droplet and particle size estimated to be 2.8 μm and 310 nm, respectively).[7] The aerosol was introduced into a horizontal twin-zone tubular flow reactor with compressed air as a carrier gas. The airflow rate was 0.1 m^3/h. The heated region was 1.3 m long, 3.2 cm dia of the quartz tube, with $T_{max} = 1173$ K in both reaction zones. The droplet/particle velocity was 0.035 m/s. Three charges of powders were collected — after the first heated zone (powder charge 1), the second one (powder charge 2) and from the collecting chamber (powder charge 3). The droplet/particle residence time was calculated from the carrier gas flow rates and the geometry of the reactor. In the case of the powder charge 1 the aerosol residence time was 3 s at 1173 K. After the powder was trapped, hot air (973 K) was flowed over the powder sample for an additional 16 h. The residence time for the powder charge 2 at 1173 K was 6 s. In a similar way as for charge 1, after the powder charge 2 was trapped, hot air (673 K) was flowed over the powder sample for an additional 16 h. The powder charge 3 has residence time of 38 s at 1173 K.

Thermal analyses of the precursors and synthesized powders were performed using DSC (detector type Shimadzu DSC-50) and DTA (detector type Shimadzu DTA-50). The analyses were performed in nitrogen atmosphere at a heating rate of 10°C/min. Particle size distribution analysis was performed by a laser particle size analyzer (Malvern Master Sizer). One-hundred milligrams of powders were used for analysis, ultrasonically deagglomerated and suspended in a referent solution (0.05% sodium hexametasulphate water solution). Crystal phases in the synthesized samples were revealed by X-ray powder diffraction using a Philips PW 1710 automated powder diffraction with CuK_α radiation with the step-scanning mode of 0.02°/1 s. Compositional homogeneity and particle morphology of obtained particles was determined by SEM (Horiba S-4500) with an X-ray Microanalyzer (Horiba EMAX-7000). For that purpose, powder samples were sputtered with Au (Au depth layer 150 Å made by Quick auto Coater JFC 1500). Qualitative and semiquantitative sample analyses proceeded in accordance to spot (analyzing area 100 Å, beam depth 50 nm) as well as square analysis.

3. Results and discussion

DSC and DTA curves of the starting components and synthesized powders are shown in Fig. 1. DSC analysis of the mixture precursor salt shows three main phenomena: (a) melting of metal nitrate salts at temperatures 306 and 341 K; (b) losing of crystal water, denoted in accordance to an expanded endothermic peak around 382 K; (c) nitrate decomposition which begins around 410 and ends at 570 K. The results of DTA measurements of the synthesized Zn–Cr–O powders do not show any of these effects.

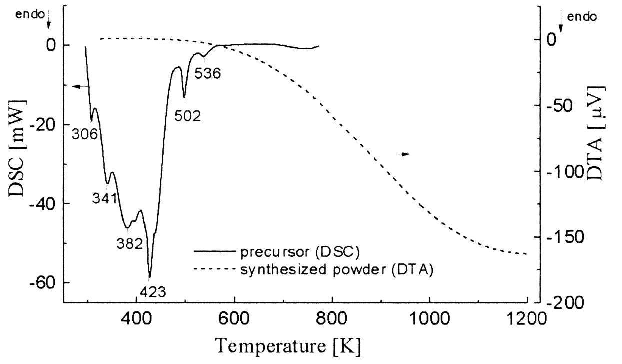

Fig. 1. Thermal analysis of the precursor solution and synthesized Zn–Cr–O powder.

Particle size measurements, performed for all investigated samples, did not show any influence of the residence time on the particle size distribution in the investigated range. The particle size distribution is log-normal with the mean particle size, D_{50}, estimated to be 470 nm (Fig. 2). The calculated particle size is smaller than the measured values for around 40%. The observed discrepancy is presumably the consequence of the irregular shape of particles rather than the particle porosity, as observed in accordance to the SEM examination (Fig. 3). The SEM photograph of the powder charge 3, after the residence time of 38 s (Fig. 3c) revealed a composite particle structure. Each particle represents an agglomerate of smaller grains, less than 70 nm in size. The agglomerated particles exhibited spherical morphology and grains are loosely sintered. In some cases, different phases are easily revealed at the particle surface as a result of an incomplete reaction. After 16 h of hot gas (973 K) flowing over the powder charge 1, the particle morphology is completely different (Fig. 3a). Individual, irregular shaped particles with a smooth particle surface indicating that the surface reaction has been completed are revealed.

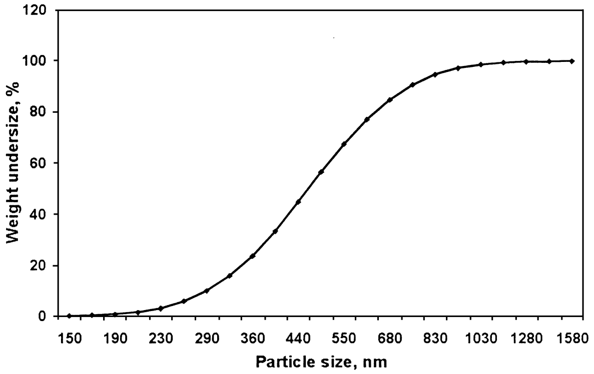

Fig. 2. Particle size distribution for zinc–chromium common nitrate solution decomposed at 1173 K in accordance to aerosol synthesis (powder charge 1).

Particle bonding and neck formation, denoting initial interparticle sintering, can be observed as well. However, for the case of the powder charge 2, where the residence time is 6 s, and after exposure to the flowing hot air stream (temperature of 673 K, $t = 16$ h) the particle morphology exhibited the presence of both smooth,

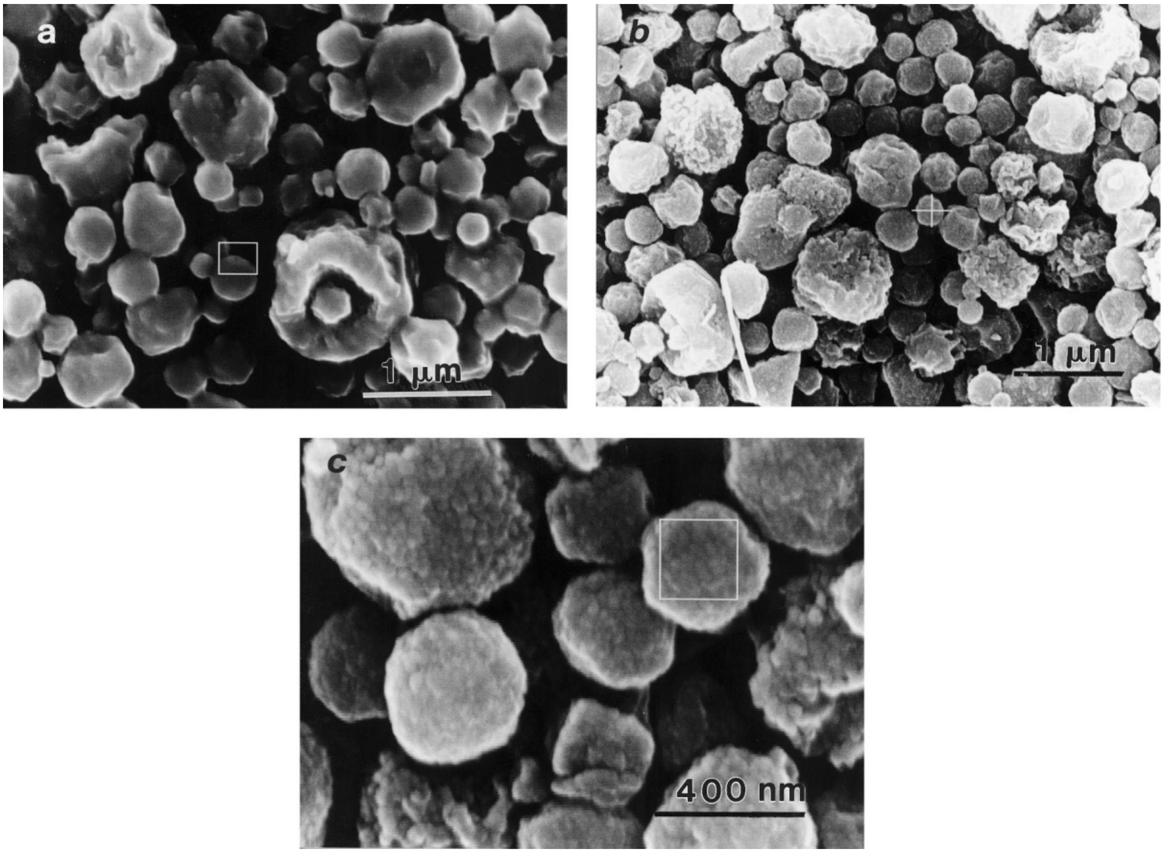

Fig. 3. Scanning electron micrographs of the powders obtained from the zinc–chromium common nitrates solution decomposed at 1173 K in accordance to aerosol synthesis: a (powder charge 1): b (powder charge 2); c (powder charge 3).

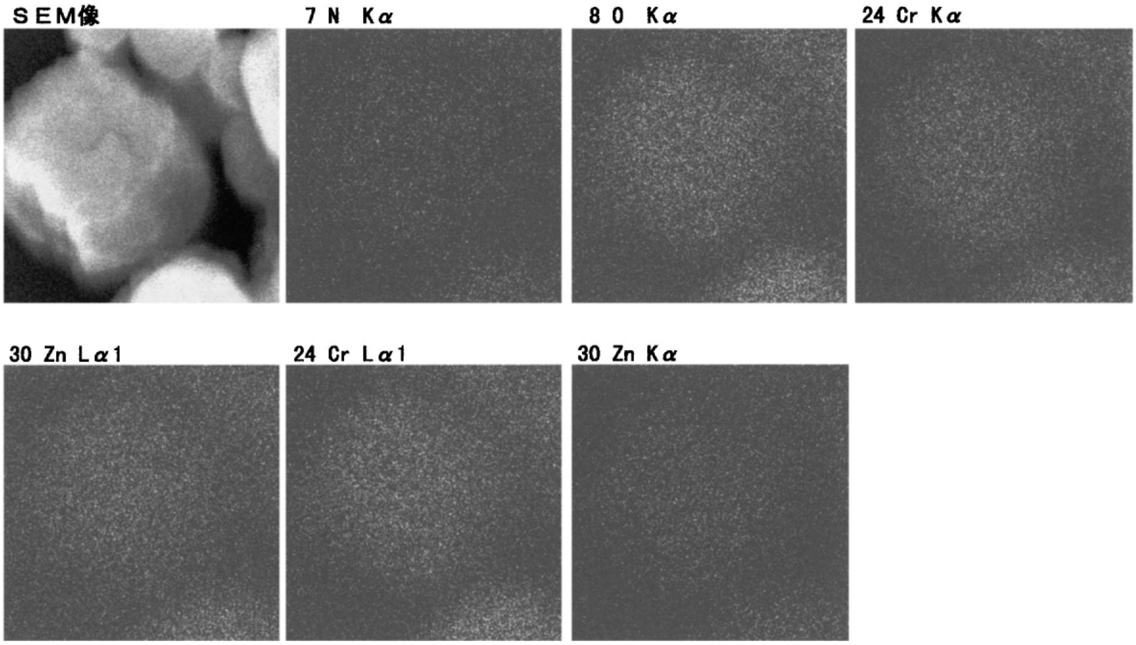

Fig. 4. EMAX distribution of the constitutive elements in a 500 nm sized particle.

aggregate free particles as well as composite ones, with small grains less than 40 nm (Fig. 3b).

EMAX mapping for synthesized samples proved uniform distribution of the constitutive elements inside the examined particles: zinc (Zn Lα, Kα), chromium (Cr Lα), oxygen (O Kα) and nitrogen (N Kα), as presented at Fig. 4. The results of semiquantitative EMAX analysis indicate very similar chemical composition for all examined particles with the mean Zn/Cr concentration ratio at 0.7±0.03. There is no clear and biased evidence about the influence of the particle residence time on Zn/Cr concentration ratio.[8] The obtained value denotes that the solution concentration ratio (0.5) is not fully achieved in the resulting particles. However, EMAX analysis also revealed some nitrogen content in all investigated samples, as a result of incomplete decomposition.

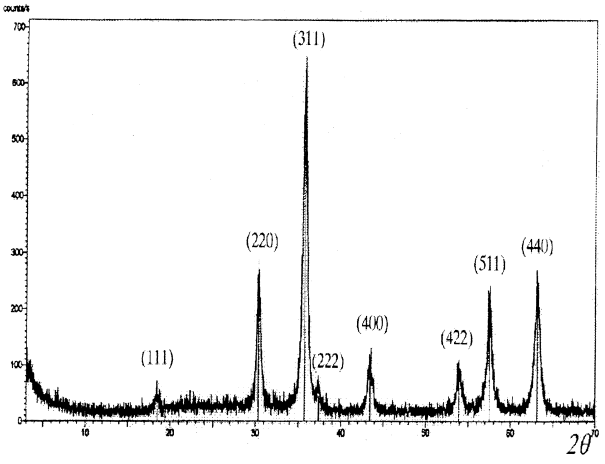

Fig. 5. X-ray diffraction patterns of the synthesized Zn–Cr–O powder (charge 1).

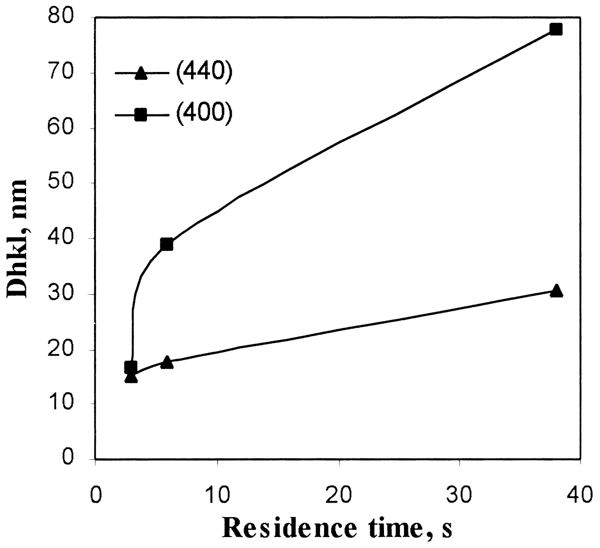

Fig. 6. Change of the average crystallite size with residence time.

Qualitative X-ray diffraction analysis showed the presence of a single crystal phase spinel $ZnCr_2O_4$, in all examined powder charges. Typical XRD patterns for the samples are shown in Fig. 5. Many peaks are very broad owing to the fact that the primary crystallite size in the powder samples is rather small. The average crystallite size was estimated for diffraction lines (400) and (440) of the spinel phase in accordance with Scherer equation.[9] The zinc chromium oxide particles were composed of primary nanocrystallites smaller than 70 nm. The structural changes expressed through the crystallite size imply gradual increase of crystallinity with increasing of the residence time during synthesis (Fig. 6).

4. Conclusion

Ultrasonic (1.7 MHz) spray pyrolysis is used for the synthesis of fine, 470 nm sized zinc chromium oxide particles from the corresponding metal nitrates solution with the mean aerosol droplet size of around 2.8 μm. The aerosol decomposition proceeded at 1173 K by changing the aerosol residence time from 3 to 6 s. The influence of different decomposition schedules on the particle chemical content and morphology was examined. A composite particle structure is revealed after the residence time of 38 s, while after the samples were additionally exposed to a hot gas stream, the surface reaction proceeds more rapidly and consequently the particle morphology is characterized by the presence of individual, irregular shaped particles with a smooth particle surface. EMAX analysis proved homogeneous distribution of elements. It was shown that the chemical content with the mean Zn/Cr concentration ratio around 0.7 does not depend on the residence time for the investigated range.

Acknowledgements

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