Theoretical Aspects of Structural Design of Various Metal Powders Obtained by Ultrasonic Spray Pyrolysis

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Abstract. This article review a theoretical aspects of structural design of various metal powders model describing the way in which a structure and substructure of various metal powders at the different hierarchical level can be designed, has been broadly discussed. Besides, the values of so obtained basic structural parameters (particle and sub-particle size distribution) with experimentally obtained values have been compared. This model also defines population balances for each line in the size distribution spectrum, thus showing that the process of the particle genesis (its structure and substructure) is fully determined by harmonization between the physical fields (external, ultrasound field and internal field, inherent to the system as the consequence of its geometry and its physical characteristics). This approach ascertains that some unique properties of any system, very typical for its low level of structural organization (e.g. confined physical properties) can be retained in the process of enlargement of sub-elements into much bigger macro-ensembles (macro-blocks). Consequently, it is possible to retain their individuality in any structural level. In this paper is shown that this approach, applied in the our previous investigations to numerous ceramic materials, like SiO_2, Al_2O_3, mullite, cordierite and TiO_2, gadoliniumsilicate, ytriumsilicate, calciumsilicate doped with rare earths, and calciumhidroxyapatite, phosphorous doped tungsten bronzes etc, can be successfully applied to the investigations of various metal powders such as Cu, Co and Ag powders obtained by ultrasonic spray pyrolysis-USP method.

Introduction

Metal's nanostructured powders exhibit unique properties that are different from those of the bulk metals, due to quantum size effects. The mechanical, catalytic, magnetic, electric and conducting properties of nanostructured metal powders can be greatly varied only by changing the particle size, without changing their chemical composition. Advances in controlling particle size distribution and surface properties of metal powders opened up the possibility for their catalytic, electronic and medical applications.

Fine nanosized Ag-particles were used by Ide et al.[1] as a reference material to consider the effect of particle size on bondability. Showing complete new characteristics and behaviors, nanosized metal are opening new product innovations for environmental protection (e.g. for wastewater treatment). Therefore, various techniques have been used in processing of metal oxide systems and subsequently their reduction in metallic system, with the general request to obtain as much as smaller particles of the metal powders. These techniques include sol-gel methods, hydrothermal methods, mechanochemical methods, to mention just few of them. Among many of them, as one very promising methods which can be successfully combined with some of previously mentioned is spray pyrolysis method.

In this paper, various metal powders such as Cu, Ag and Co powders, obtained using Ultrasonic Spray Pyrolysis (USP) method were presented. The experimental evidences obtained by using different metal precursors and temperature treatment during USP were mutually compared. In order to fully describe the mechanism of USP and estimate the influence of applied physical fields to the

development of nanostructure of these metallic powders, the additional analysis of obtained experimental data has been made using break-up model of capillary waves. This model has been developed by V.Jokanovic[2-4], and successfully applied to the numerous ceramic systems, such as mullite, alumina, cordierite, titaniumdioxide, siliciumdioxide, calciumhydroxyapatite, gadoliniumsilicate, ytriumsilicate, calciumoxyapatite, pseudowolastonite, phosphorus doped tungsten bronzes etc.

Experimental

The solutions of $AgNO_3$ (0.1 mol/l), $CuSO_4$ (0.05 mol/l and 0.3 mol/l) and $Co(NO_3)_2$ (0.04 mol/l) were prepared by dissolution of equivalent amounts of the corresponding salts in deionized water. They are used as precursors to obtained metallic powders of Ag, Cu and Co in the USP method by procedure published elsewhere[5-7].

This method has been done using laboratory setup consisted from ultrasonic atomizer of aerosol generation (RBI transducer) with one transducer operating at a frequencies of 0.8 MHz (for Ag, Co and Cu powders with c_p =0.05 mol/l and c_p=0.04 mol/l), and 2.5 MHz (for Cu[*] powder, c_p=0.3 mol/l). The reaction chamber-furnace equipped with quartz tube were exposed to the temperature of $1000\,^{\circ}C$ (for Ag, Co and Cu precursors treated at 0.8 MHz) and $800\,^{0}C$ (for Cu[*] precursors treated at 2.5 MHz). The flow rate of the gas carrier (N_2+H_2) was 0.022 ls^{-1}

The size distribution of metal spheres was analyzed with semiautomatic image analyzer (Videoplan, Kontron) connected to the scanning electron microscope (SEM, JOEL 5300).

Theoretical model of particle structure design

Force frequency of the ultrasound oscillator induces equivalent waves in the given liquid column, in direction perpendicular to direction of disturbance (transversal waves) and in direction parallel to direction disturbance (longitudinal waves).

In general, formed standing waves are ellipsoidal, basically determined by the relationship between the damping factors for transversal and longitudinal waves, depending very much on thickness of the sprayed solution liquid column.

Beside that, size distribution of the aerosol droplets is influenced by physical characteristics of that solution (surface tension and viscosity), and geometry of the vessel containing the solution. For sufficiently thin liquid columns, damping factors of transversal and longitudinal waves differ only negligibly, due to obtained standing waves which are spherical. In case of the ellipsoidal form, standing wave can be represented in the form of Laplace equation, expressed in polar coordinates:

$$\rho \frac{\partial^2 \varphi}{\partial t^2}\bigg|_{r=R} - \frac{\sigma}{R^2}\left\{ 2\frac{\partial \varphi}{\partial r} + \frac{\partial}{\partial r}\left[\frac{1}{\sin\theta}\frac{\partial\left(\sin\theta \frac{\partial\varphi}{\partial\theta}\right)}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2\varphi}{\partial\varepsilon^2} \right] \right\} = 0, \tag{1}$$

where r is radius of the aerosol droplet, ε and θ are angles corresponding to equation transformed in polar coordinates. Solution of the given equation gives the set of radius dimensions equivalent to given wave-damping factor:

$$d = \frac{1}{\pi}\left(\frac{2\sigma\pi}{\rho f^2}\right)^{\frac{1}{3}}\left[l(l-1)(l+2)\right]^{\frac{1}{3}}, \tag{2}$$

where l is integer, taking the values $l \geq 2$.

Based on obtained discrete values of aerosol droplets size in size distribution spectrum, mean powder particle size can be calculated from the following equation:

$$d_p = d_n \left(\frac{c_{pr} M_p}{\rho_p M_{pr}} \right)^{\frac{1}{3}}$$

(3)

where d_p is powder particle diameter, ρ_p is powder density, M_p is powder molecular mass, c_{pr} is precursor concentration (solution used for spraying when forming powder particles) and M_{pr} is precursor molecular mass.

Results and discussion

In order to determine interrelation and agreement between the theoretical model, defining discrete values in the distribution spectra for the metal powder particles-MP and their corresponding constitutive smaller elements subparticles- MSP the experimentally determined values (diameter values for the mean-sized particles and their belonging subparticles) were first analyzed. The analysis follows the complete distribution spectrum for the MP and the MSP with their population balances (balances for each value contained in that spectrum), as it is presented in Fig 1.
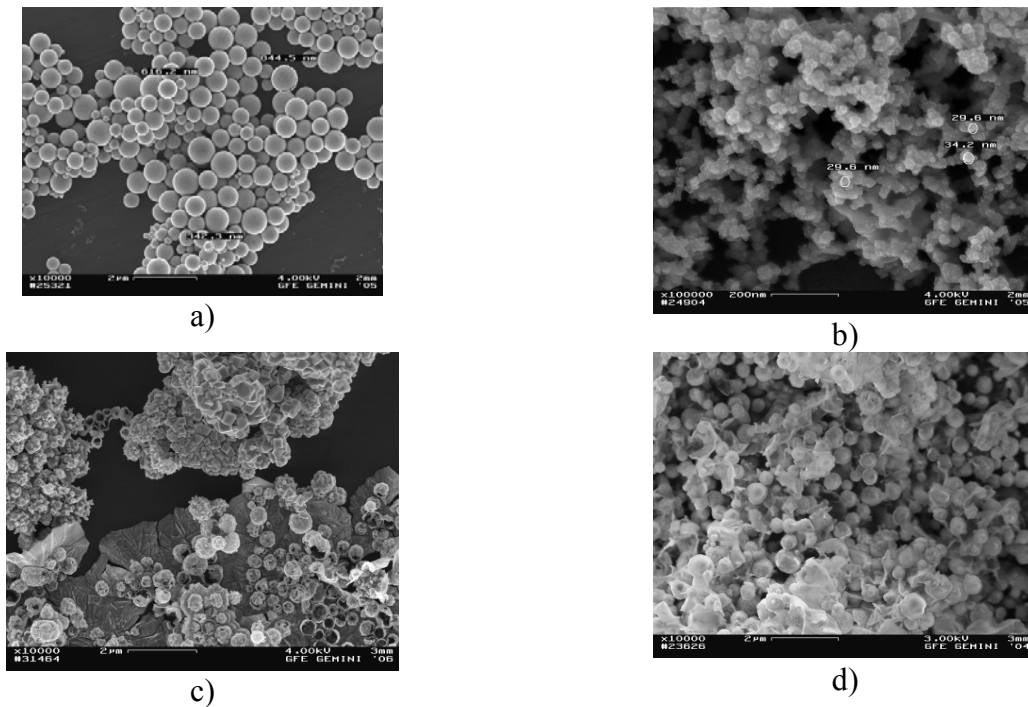

Fig. 1. Typical morphology of a) Ag, b) Cu, c) Cu* and d) Co metal powders

Experimentally obtained data (see Fig.1.) were compared to the theoretically estimated values before and after statistical processing, using computer program ORIGIN 5. The obtained results for the mean particle size are almost identical independent on the distribution function used for data fitting Gaussian ($_G$), Lorencian ($_L$) or Voight ($_V$) ($d_G = d_L = d_V = 0.66 \pm 0.05$ μm for Ag; $d_G = d_L = d_V = 0.025 \pm 0.004$ μm for Cu); ($d_G = 0.555 \pm 0.002$ μm, $d_L = 0.548 \pm 0.002$ μm and $d_V = 0.555 \pm 0.003$ μm Co). Similar results are obtained by comparing population balance of MP particles (populational balance corresponding to the Gaussian, Lorencian and Voight maximum was 0.15 for Ag; Gaussian maximum 0.43 for Cu, while Lorencian and Voight values were physically unacceptable (values 1.04); Lorenzian and Gaussian maximum was 0.29, the balance corresponding to Lorenzian maximum was 0.33, and balance corresponding to Voight maximum was 0.29 for Co).

In the case of Cu[*] it has been shown that above mentioned statistical functions can not be useful. Therefore it has been applied a FFT filter of Savicky-Goley smoothing procedure to calculate mean value of diameter, which was in this case $d_{FFT}=0.59\pm 0.01\mu m$. The calculated values are in good agreement with determined mean values of diameters corresponding powders which were 0.63 μm for Ag, 0.024 for Cu, 0.50 for Cu[*] and 0.52 for Co.

The calculated theoretical values of particle diameters were as follows: 1.23 μm for Ag (0.63 μm experimental value), 0.69 μm for Cu (0.024 μm experimental value), 0.69 μm for Cu[*] (experimental value 0.5 μm) and 0.50 μm for Co (experimental value 0.52 μm).

Based on the above mentioned results it appears that in the case of the Ag the precipitation is exceptionally made by surface precipitation mechanism, and the spheres of Ag were hallowed. It is possible easy to calculate depth of their walls. That can be caused by very high temperature of thermal treatment of this system, which cause of blow-up and probably melting of Ag solid particles in the part of the highest temperature in the furnace. That can cause such almost ideal spherical shape of their particles. The mean depth of the Ag hallow sphere is 0.325 μm. Inside, in the center of the sphere calculated radius of void is 0.29 μm.

In the case of the Cu calculated value, the mean diameter of its particles (0.69 μm) is much smaller (0.024 μm) than it was expected. The values of the Cu particle diameters correspond to the expected values of its subparticles, which are of this order of magnitude. Certainly, the subdroplets particles which include subelements of the droplets, have values close to 155 nm (basic value) as well as some droplets with a higher values. Therefore, it seems that droplet of Cu-precursor has been exploded and broken to the subdroplets and then solidified. That is very interesting and unusual behavior of systems during spray pyrolysis. The other two cases are typical. In the case of Cu[*], smaller particles were volume precipitated, and the largest were partially surface precipitated (therefore, a small difference in the experimental and theoretically estimated values for this system).

The agreement for Co particles is almost completely (theoretical and experimental values of particle diameters were 0.50 μm and 0.52 μm, respectively). This system was entirely volume precipitated. The comparison between the experimentally measured and calculated determined values of the particle diameters are presented at Fig. 2.
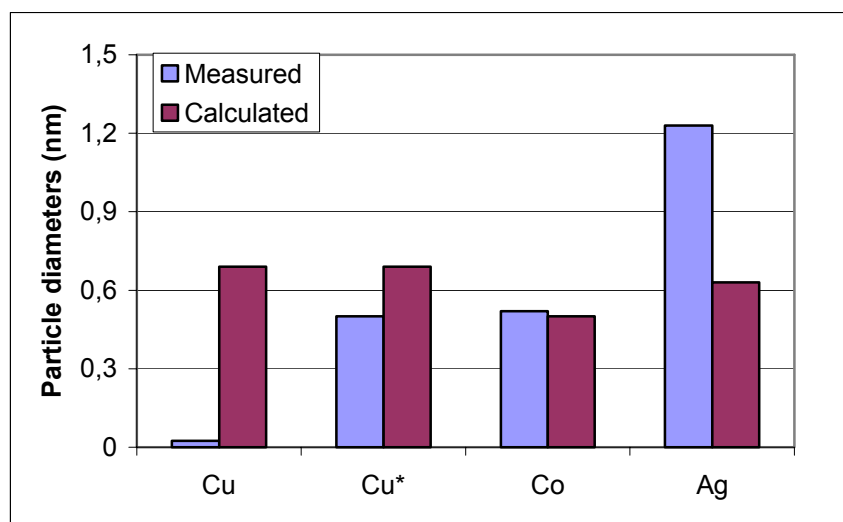

Fig. 2. Comparative analysis of measured and calculated particle diameters

Based on the all previously mentioned it is obvious that only synergy between theoretical understanding and mathematical modeling should give a complete picture about the ultrasonic spray pyrolysis process.

Conclusion

In this article, quantitative analysis of structural and substructural elements of metallic Ag, Cu and Co powders (particles/hollow sphere) by their mean diameters, size distribution (for the secondary particles), belonging discrete values of individual particle diameters and their population balances is presented.

It was found, that theoretical model of structural and substructural design successfully describes the system from the aspect of its basic design elements. The theoretically estimated values (mean particle diameter, distribution of particles/hollow spheres, population balance, size of substructural design elements), are in the satisfactory agreement with experimentally determined values. Investigations of these systems showed that is possible:

- To keep initial properties of the system unchanged during design of the system (colloidal solution) on the higher level
- To determine, based on theoretical estimates, final design of the system (on secondary particle/hollow sphere level) and its subdesign

Theoretical model is independent on selected system, so it is of the general value; being conceived as a model of correspondence between internal and external periodical physical fields, appearing in the system due to the given excitation, it could be also applicable in other processes developing in periodical physical fields (syntheses assisted by various plasma types-radio frequent/microwave and processes occurring in high-energy mills or initiated by high-energy explosion waves).

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