NANOPARTICLES PRODUCTION VIA SPRAY PYROLYSIS. HEAT AND MASS TRANSFER AND PHYSICAL-CHEMICAL TRANSFORMATIONS

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One of most effective and cheap methods of nanoparticles production is the spray pyrolysis. Essence of spray pyrolysis is the obtaining nanoparticles from evaporating microdroplets of salts solutions. This continuous method is well suited for semi-industrial nanoparticles production.

A wide variety of different metals, metal oxides and alloys nanoparticles have been already obtained by researchers and engineers of Japan, South Korea, USA and many other countries [1]. Shape of this nanoparticles can be pure spherical, there are sometimes agglomerates of nanoparticles or a hollow submicron structures.

We present here the basic results of our decade long experimental and theoretical researches of the heat and mass transfer processes which determine the efficiency of the spray pyrolysis [2-3].

The central process is the evaporative cooling of femtoliter droplets of the salt solution. The rate of evaporative cooling depends on several important parameters as flow rates of carrier gas and sprayed solution flow rate, a wall temperature and the total gas pressure in the of an aerosol reactor. Typically cooling rate is about 10^4 K/s. It is worthy to emphasize that not only solvent molecules evaporate but also some molecules of intermediate substances in the solution. Spontaneous formation of molecules intermediate substances is due to salts dissociation and their interaction with a solvent.

During evaporative cooling of the droplet a supersaturated solution of initial salt is formed inside the droplet. The spatial scale of heat and mass transfer processes is several microns.

Supersaturated solution inside the droplet decays via nucleation. Finally, several nanosized clusters are formed. These clusters are situated stochastically in the droplet. Growth of these clusters is governed on the scale of several nanometers.

Chemical kinetics of a transformation of the original salt takes places on the interface of these clusters with solution. The rate of transformations depends on the evaporation rate of intermediate substances from droplet surface and a rate of solid state diffusion of atoms in the clusters. The interconnection of these two processes determines the rate chemical transformation during spray pyrolysis. The crucial circumstance that a diffusion coefficient is a solid phase is smaller of a diffusion coefficient in liquid on three orders of magnitude, therefore there are some limitations on efficiency of the method of spray pyrolysis. The efficiency decreases if the droplet radius is more than several microns. Typical engineering solutions of overcoming these misbalances are: increasing of the wall temperature in aerosol reactor or decreasing total pressure in the aerosol reactor. Both engineering solutions increase the rate of the droplet evaporation.

The residence time of liquid droplets in the aerosol reactor effects on morphology of a nanoparticles ensemble in the droplet. The main physical processes are the Brownian diffusion and coalescence of nanoparticles. It was shown that if the residence time is above 10 milliseconds then the final product of the spray pyrolysis is a one submicron nanoparticle. The reason is that the vast majority formed nanoparticles are dissolved and products of these process deposit on the biggest nanoparticle. The Brownian diffusion distributes nanoparticles in the droplet practically spatially uniformly if droplet evaporation rate is not high one. It was established in our researches that for high evaporation rate the contribution of the Brownian diffusion is weak and hollow structures emerge due to the agglomeration of nanoparticles and subsequent growth near the droplet interface.

Further development of the spray pyrolysis method of nanoparticles production of different compositions will be based not only technical experiments, but on deep understanding of all heat and mass transfer processes, which open ways for the full control of this method and its possibilities.

References

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