Scale Up of Ultrasonic Spray Pyrolysis – First Results for Synthesis of nanosized Particles

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1 author:

Jelena Bogovic
VTU Engineering Deutschland

Scale Up of Ultrasonic Spray Pyrolysis - First Results for Synthesis of nanosized Particles

J. Bogovic[1], G. Matula[2], S. Stopic[1], R. Rudolf[3], B. Friedrich[1]

[1]IME Process Metallurgy and Metal Recycling, RWTH Aachen University, Aachen, Germany

[2]Elino Industrie-Ofenbau GmbH

[3]Faculty of Mechanical Engineering, University of Maribor; Slovenia

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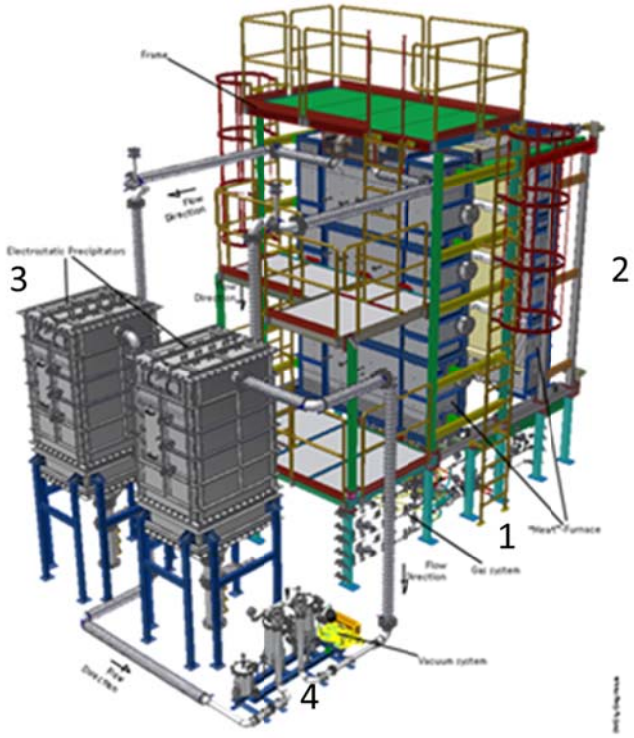
Abstract

Nanostructured materials and their application have been attracted much attention in the last decades. Due to extended research in this area, various nanomaterials and endless application of them is known today. This led to rising demand for methods suitable for big scale nanomaterials production, especially when it comes to ones with target morphology, complex composition, multi-component and coated materials. In this paper a report of first results on scale up of Ultrasonic Spray Pyrolysis (USP) process is presented, which is relatively inexpensive and quite versatile technique for nanoparticle production based on an aerosol process. It is possible to produce fine metallic, oxidic, composite nanoparticles of precisely controlled morphology and defined chemical compositions from water solution using different metal salts and their mixtures. In the first trial on big scale USP equipment nano Ag powder was produced [1-4]

Introduction

One decade of the experience in nanoparticle synthesis by USP at the IME Process Metallurgy and Metal Recycling, RWTH Aachen University was the basis to develop device on an industrial scale for nanoparticle production. The goal of this scale up project was to develop the equipment that is going to be on the one hand suitable to produce larger quantities on nanoproducts, and that is on the other hand going to be flexible and suitable to produce nanopowders with various morphologies (spherical, cylindrical, triangular, dense, porous, hollow, core/shell nanoparticle). The equipment - financed mostly by the DFG Deutsche Forschungsgemeinschaft and Land NRW in frame of the program "Forschungsgeräte" and with 10% self-investment, was constructed in such a way that main process steps maintain the same like in the lab scale equipment and that it is possible to control the same process parameters. The main process steps by USP are: evaporation of solvent, diffusion of solutes, precipitation, decomposition and densification. [5] The main parts of the equipment are: 1-Aerosol ultrasonic generator, 2-High-temperature furnace with five wall heated reactors, 3-Electrostatic filter and 4-Vacuum system. The concept draft and device photo are shown in Fig. 1.



Dimension: 5m x 12m x 6m
Aerosol: 5 generators (3 transducers each)
Furnace: 4 Heating Zones (max. 1000°C)
Reactors: 5 Stainless steel pipes (0,6 x 3,6m)
Collection: 2 electrostatic filter
Vacuum pump: operating pressure in system 960mbar

Figure 1: The concept of demo scale USP: 1-Aerosol ultrasonic generator, 2-High-temperature furnace with five wall heated reactors, 3-Electrostatic filter, 4-Vacuum system (left) and photo of the equipment (right) [6]

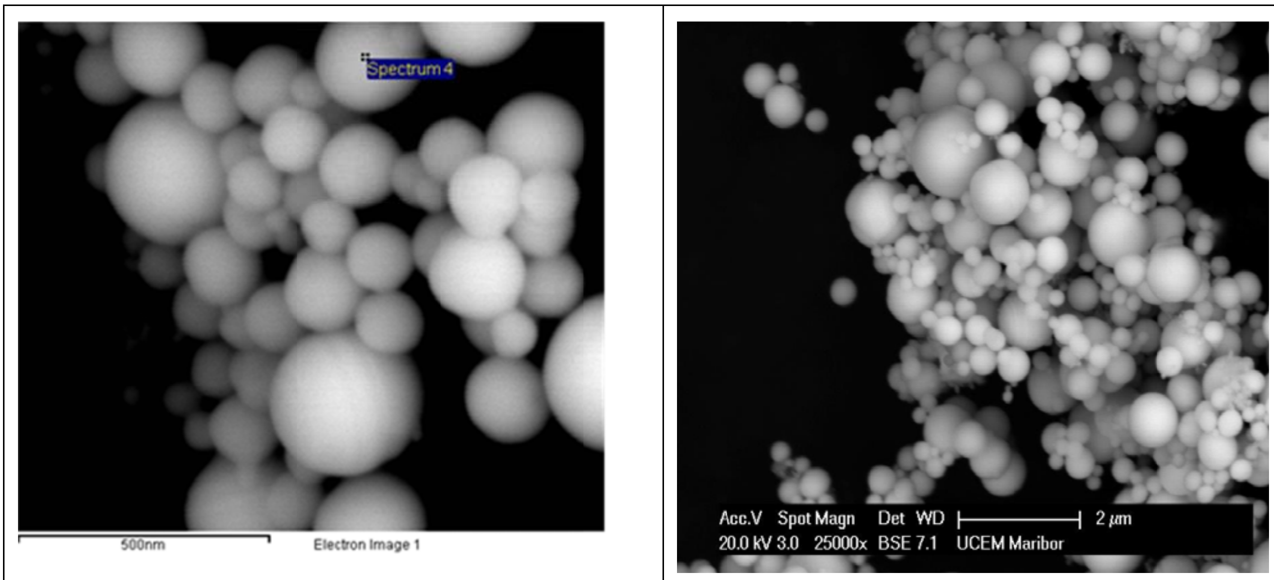
Experimental

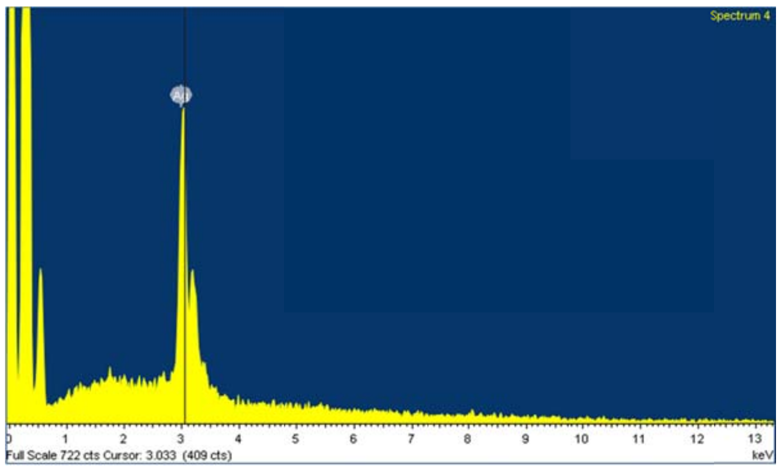
The large scale USP equipment design is the result of joint work of IME researchers and engineers from Elino GmbH. The transfer of scientific achievements, maintain of process parameters, involvement of prototype devices, maintain of equipment flexibility and resistivity to all working surroundings were only some of the engineering challenges. As mentioned before, the USP equipment can be divided in four main parts. The first part is gas system and 5 aerosol generators. Gas system is suitable to control volume (mass-) flow of pure and pre-mixed gases (0,5-3,5m³/h) and on this way provide carrier and reaction gas for the process. Aerosol generators are result of joint work of IME researchers, engineers from Elino (Düren, Germany) and PRIZMA (Kragujevac, Serbia). The advantage of this system comparing to other systems for aerosol production are: small droplet size, industrial design, continual process, corrosion resistivity, tightness and automatically regulation. The furnace consists of 4 separately regulated heating zones. In the furnace 5 wall heated stainless steel reactors are placed, where there is possibility to take online-probes from each heating zone from one of reaction pipe (special construction). Produced powder is collected in two electrostatic filters (each consists of 12 collecting electrodes), where each of them is equipped with special hammer system which enables to “pour” nanoproduct into tight containers under each filter. Equipment detail and scale up process was detailed topic in one of the previous reports. [6]

First tests were conducted in the last quarter of 2012 with a goal to test functionality of all equipment parts, control of process parameters and stability of the process. In those tests all process parameters such as temperature, volume flow of carrier gas, pressure, precursor level regulation and high voltage were tested with its minimal and maximal value and stability of it was monitored during the time. After those tests without nanopowder production were evaluated as successful, the “real” synthesis of nanosized silver particles was conducted.

This experiment was done with a silver nitrate as a precursor solution, air was used as a carrier gas, with a flow rate of 60 l/min for each reactor, which means that a carrier gas flow through a whole system was 300 l/min. Furnace temperature was regulated for each heating zone: 500-800-1000-1000°C (first, second, third and fourth heating zone) and pressure in the whole system was -40 mbar (+/- 5 mbar). Chosen temperature profile had two main purposes: provide a heat for thermal decomposition of silver nitrate to elemental silver ($AgNO_3 \rightarrow Ag + NO_2 + 1/2\ O_2$) and to provide a heat for mentioned process steps related to particle formation (evaporation of solvent, diffusion of solutes, precipitation and densification). [7] Complex influence of temperature profile, precursor concentration, carrier gas flow rate and the retention time on particle formation and morphology was subject of studies in the past decade. Process parameters for this experiment were chosen based on previous experience. [7-10]. The first experiment was conducted as a continual test, the total duration time was 36 hours (heating phase of furnace app. 4h, the rest is reaching steady state and nanopowder production). During the test, process parameters that have direct influence on nanopowder synthesis were successfully kept constant. This is very important for product homogeneity during the time. The most sensitive part of the equipment was determined to be electrostatic filter (particle collection system). The process window for optimal function of electrostatic filter is very small and defined by few parameters: temperature, gas kind and humidity, physical characteristics of collected powder, volume rate, voltage and thickness of collected powder layer. This part of the equipment requires further optimization in order to achieve its full efficiency.

Produced silver powder was analyzed in order to determine its structure and chemical composition. SEM and EDS results are presented in Fig. 2.





Spectrum processing :
No peaks omitted
Processing option : All elements analyzed (Normalised)
Number of iterations = 1

Element	Weight%	Atomic%
Ag L	100.00	100.00
Totals	100.00	

Figure 2: SEM Images of produced silver particles (up, left and right) and EDS spectrum of analyzed particles

As it can be seen, ideally spherical silver particles were produced. Particle size lies in the range 100 nm up to submicron. The reason for appearance of particles also in submicron size is that the starting concentration of silver nitrate solution was relatively high (the final particle size is directly influenced by the precursor solution concentration and can be manipulated). From the qualitative analyze of produced powder, it can be determined that the retention time and temperature were sufficient for full thermal decomposition to take place.

From these first results positive conclusions can be made about process principal transfer. Further optimization and development are going to be in the direction of testing the equipment on different products and better process control in order to obtain target morphology.

Summary

10 years research have reached demo scale in synthesizing nanoparticles by ultrasonic-spray-pyrolysis. Initial tests in the five hot wall tube reactor system conducted in the last quarter of 2012 have proven the correctness of design for safety, control systems operation and such parameters as heating rate, maximum temperature, pressure control in the system and gas flow. Previous conclusions clearly show successful principal transfer from lab scale equipment onto this large scale equipment (5m x 12m x 6m). In the next phase, further optimization of the process is going to be done in order to obtain better control of nanoproduct characteristics and increase production rate. Parallel to this, the collecting and handling of the generated powder material must be optimized in order to fulfill pre-industrial standards. The full paper will be published immediately after the conference as peer reviewed paper.

Acknowledgements

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