

Scale-up of the Ultrasonic Spray Pyrolysis (USP) process for nanopowder production (Part 1)

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Nanostructured materials and their applications have been one of the key research topics for industry in recent decades. Various nanomaterials and numerous applications for them are known today, and much research has been undertaken on the use of nanopowders in the Metal Injection Moulding (MIM) process. However, the industrial application of nanomaterials is still challenged by the limited number of methods suitable for large scale nanomaterials production, especially when it comes to nanomaterials with target morphology and complex composition. This paper reports on the scale-up of the Ultrasonic Spray Pyrolysis (USP) process. The USP process as a nanoparticle production method is a relatively inexpensive and versatile technology based on an aerosol process 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 [1-4].

This paper is the first of a two-part report on the results of research into the Ultrasonic Spray Pyrolysis (USP) process. This first paper features a description of the construction of a prototype device to be launched in the production phase in the first quarter of 2013. The trial phase began in December 2012 and preliminary results show the suitability of the design, as well as the success of the scientific and engineering work of the IME Process Metallurgy and Metal Recycling team at RWTH Aachen in collaboration with engineers from Elino GmbH. The second part of the report will be devoted to the control system, the technological process itself and the results of final tests of the equipment presented.

Introduction

Over the last ten years ultrasonic spray pyrolysis synthesis has been the subject of research at the IME Process Metallurgy and Metal Recycling department at RWTH Aachen. Different organic and inorganic salts were used as precursor materials for the preparation of metallic, oxidic and composite nanopowders by ultrasonic spray pyrolysis using the equipment shown in Fig. 1a.

Synthesised powders can be divided in three groups:

1. Metals (Au, Ag, Co, Cu, Zn, Ni, Fe) [1-2]
2. Oxide (TiO_2 , ZnO, Al_2O_3 , RuO_2) [3-4]
3. Composite materials with partially core-shell structure (CuNi, FeCo, NiCo, $\text{RuO}_2/\text{TiO}_2$, $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$, C/LiFePO_4 , Au/TiO_2 , Ag/TiO_2) [4]

Next to variations in chemical composition, it is possible also to produce nanopowders with various morphologies (spherical, cylindrical, triangular, dense, porous, hollow, core/shell nanoparticle). Some of the nanopowders produced by USP are presented in Figs. 1b and 1c.

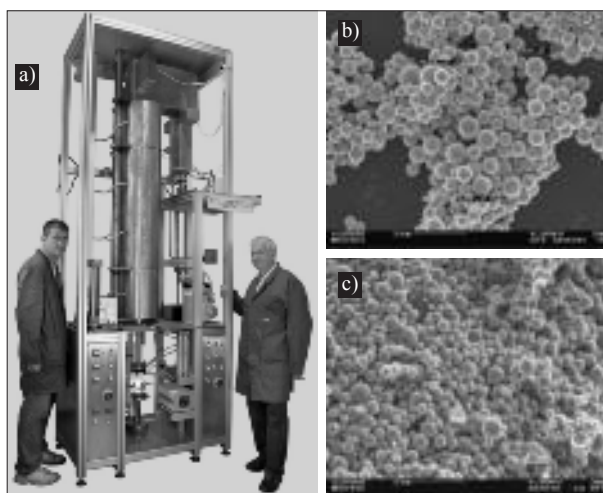


Fig. 1 a) USP Equipment at IME Process Metallurgy and Metal Recycling, b) NanoAg [2] and c) TiO_2 [4]

Design of USP equipment

A decade of experience in nanoparticle synthesis by USP was the basis to develop a system for industrial scale production. The main parts of the demonstration scale Ultrasonic Spray Pyrolysis equipment are, A: Aerosol ultrasonic generator, B: High-temperature furnace with five wall heated reactors, C: Electrostatic filter, and D: Vacuum system. The concept draft and device photo are shown in Fig. 2.

In cooperation with Elino GmbH engineers, and based on a previously built small scale prototype by the IME Institute (Fig. 1), after nearly six months of intensive work by two teams, Elino

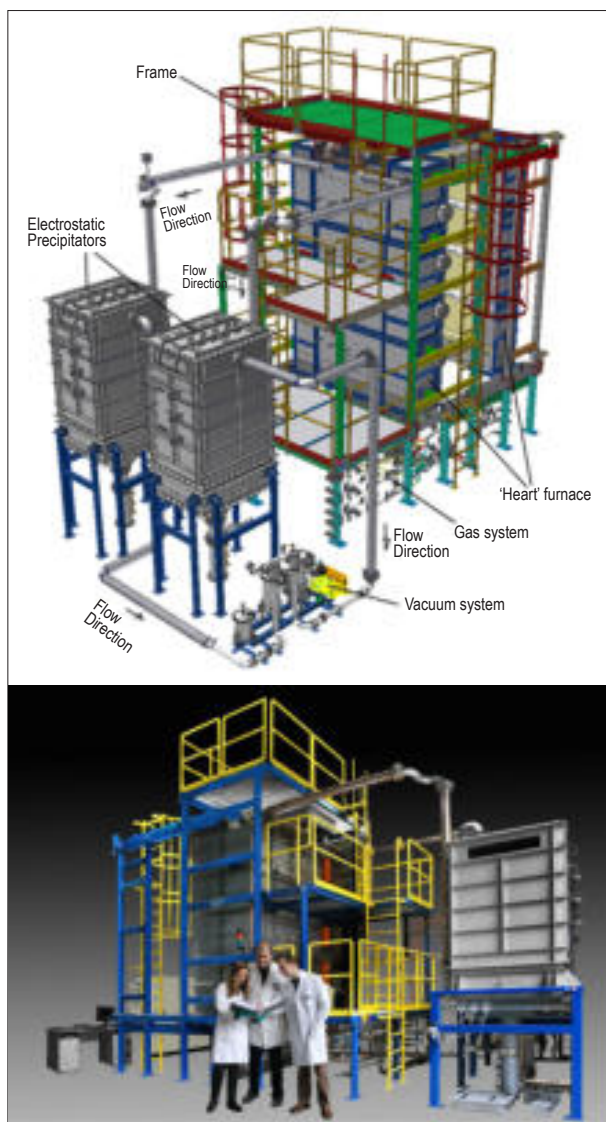


Fig. 2 The concept of Demo scale USP and photo of the equipment

GmbH and the IME Institute, the first design of the demonstration scale version of the device with the working name “MIRANDA” was developed.

The main engineering challenge was to transfer scientific achievements and maintain process specifics on a macro scale. This involved many complex calculations relating to gas flow, temperature uniformity and the impact of these factors on the process.

The “hearth” furnace consists of four separately regulated heating zones (Fig. 3). An additional unique aspect of the device is its full tightness. A specific challenge related to the thermal decomposition in an inert atmosphere (Ar , N_2), reduction (H_2) or oxidation (O_2) gases) of reaction pipes to flange connections, further affected by the negative influence of high temperatures and thermal expansion. Engineers from Elino GmbH established solutions to eliminate the above mentioned problems.

Each heating zone in the furnace is controlled separately, and each has separate temperature monitoring. Temperature uniformity is min. $\pm 10^\circ\text{C}$, max. $\pm 15^\circ\text{C}$ based on data collected after the first trials. The proper construction of heating elements and their heating power used in each of the four zones enables the setting of much higher temperatures, which additionally make this device very flexible in the full temperature range necessary for nanotechnology.

Additional advantages of this construction, following the first trials, have been identified as very good thermal insulation. At a working temperature in heating zone 2 and 3 of 1000°C , the temperature of the shell does not exceed 30°C , which ensures safe usage of delicate ultrasonic aerosol generators, which as electrical units are very sensitive to high temperatures.

Further important components are ultrasonic aerosol generators and the gas system. In order to understand the essence of the gas system, one should understand the basis of the process. A gas flow is fed to the control valve where it is adjusted depending on the type of gas or mixture of gases. Successively the gas is sucked by vacuum pump to the aerosol generators and then to the reaction pipes. This gas flow has two main functions: reaction gas and carrier gas. A vacuum pump provides the pressure below atmospheric pressure in the whole system, which has positive influence on the process itself. The gas and aerosol generation system are shown in Fig. 4.

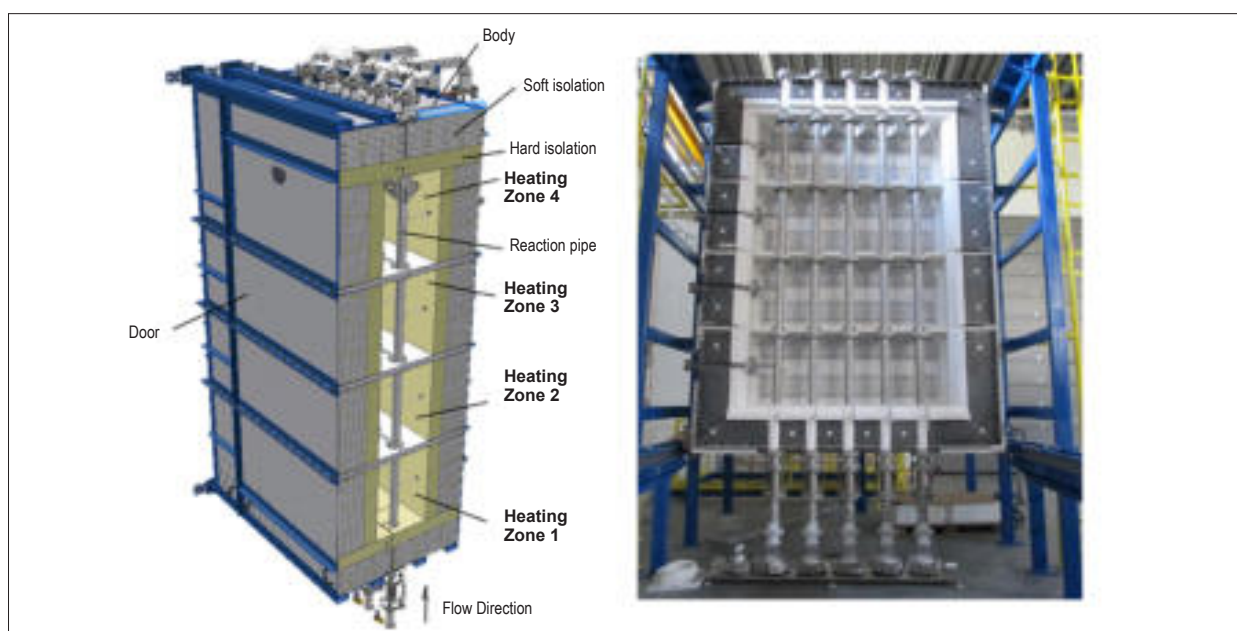


Fig. 3 Furnace with four heating zones and wall heated reactors

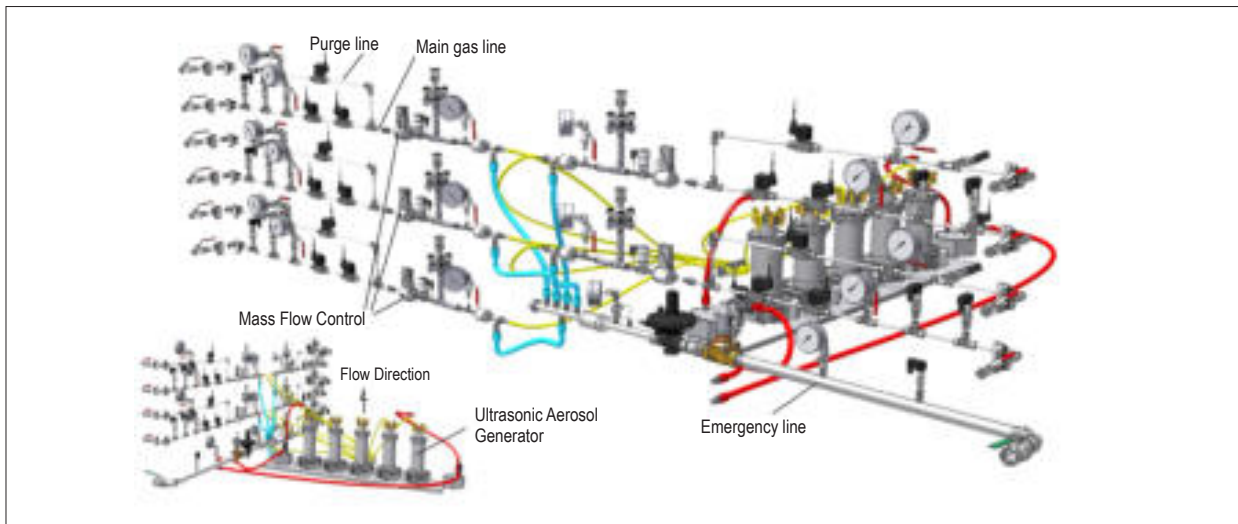


Fig. 4 The gas and aerosol generation system

There are five aerosol ultrasonic generators, called “Priznano”. Their design is the effect of the joint work between IME researchers, engineers from Elino GmbH and engineers from PRIZMA Company, Kragujevac, Serbia. The main advantages of this system compared to other systems for aerosol production are the small droplet size, established industrial design, continual processability, high corrosion resistivity and the ability to operate with H_2 .

Nanopowder collection occurs in specially designed Electrostatic Precipitators (Electro Filter). Based on the mini version and results of previous research, the IME and Elino GmbH team developed, on paper, a concept that was mathematically an extension of the laboratory design previously developed by IME and Schnick Industrieberatung. It should be mentioned that there are no exact rules on how to design or build such devices as electrostatic precipitators with regard to this particular technology. Professional involvement of members of the “MIRANDA” project showed that there is no easy transfer from the micro to macro version. Additional factors, such as the type of gasses, acids, gas flow, influence of temperature on certain materials and their nonlinear behaviour forced the engineers to reject the original version and develop an entirely new design shown in Fig. 5.

An additional factor that had an influence on the electrostatic precipitator design was making it such that it could operate with harmful gasses (which requires a gas-tight design) and acids while maintaining proper temperature inside the EGR, and simultaneously obtaining the final properties of the nano product in the required industrial quantities. It must first be clarified that this unit uses electrostatic precipitators connected to the reaction pipes coming from the furnace in such a way that redundant operation and flexible adjustment of throughput is possible. The electrostatic precipitators will always be the part of the device that requires the most maintenance and this is made possible due to the specific design.

As previously mentioned, gas and nanopowder is collected by vacuum pump from the reaction pipes placed in the furnace. The temperature of this stream is measured on the inlet to the electrostatic precipitators and is maintained automatically. This is necessary for the protection and resistance of the seal to corrosion and acids during the process.

The inner design of the electrostatic precipitator consists of a few emitting/collecting electrodes made from adequately selected stainless and temperature-proof steels.

The emitting electrode is connected to a high voltage generator

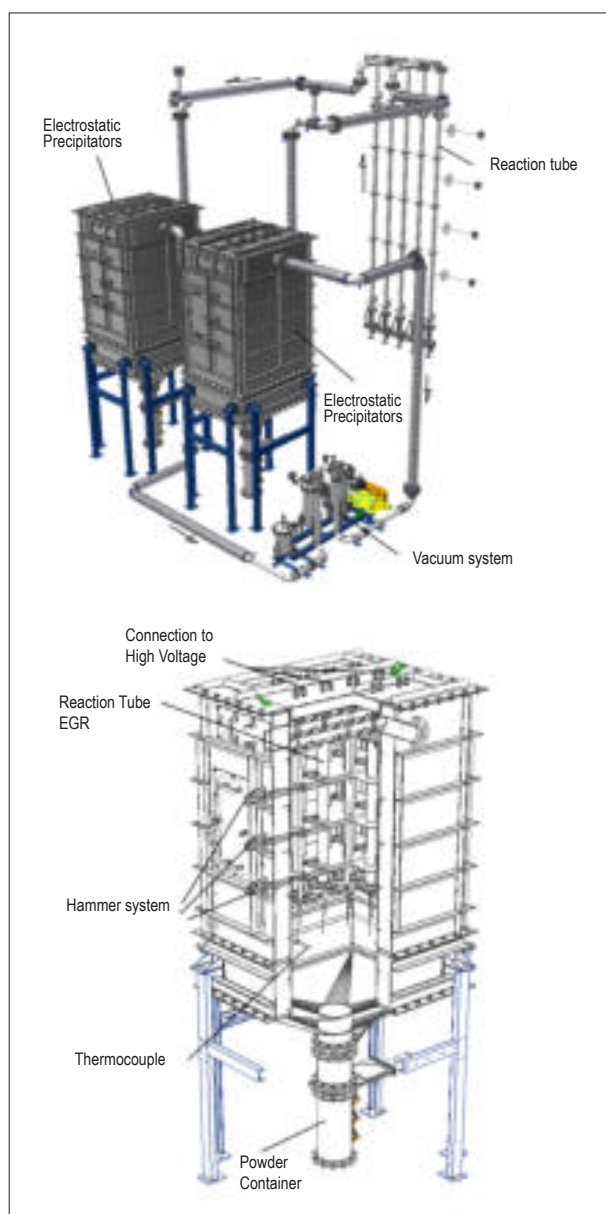


Fig. 5 Design of electrostatic precipitator

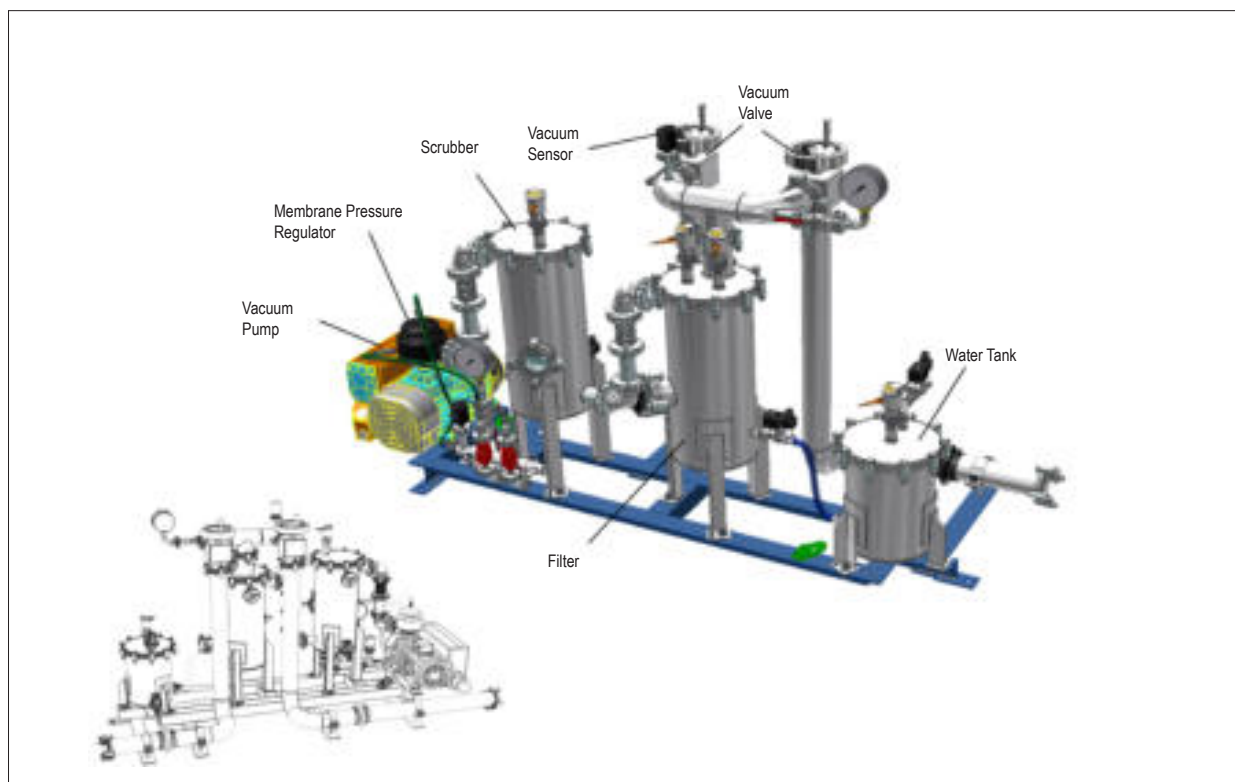


Fig. 6 The vacuum system

that creates a powerful electrostatic field. As a result, nanoparticle is kept in collection pipes and the “carrier atmosphere” is discharged to the vacuum system. It should be mentioned that pressure, flow and temperature of the gas, otherwise called the “carrier atmosphere”, have a major impact on the process. However, when the “carrier atmosphere” enters the electrostatic precipitators, there are two more additional factors decisive for obtaining the nanoparticle - the voltage that creates the electrostatic field and the geometry of the reaction pipes. In order to collect nanoparticle during production, each of the electrostatic precipitators is equipped with a special hammer system, which enables the “pouring” of the nanoparticle into containers under each EGR.

The last element of the equipment is the vacuum system, shown in Fig. 6. The vacuum system, in addition to the pump and vacuum valves, consists of two filters with a design that ensures the completely safe operation of the vacuum pump without the need for frequent oil replacement, as well as ensuring that the pump itself is not damaged by the remnants of nanoparticle in the “carrier atmosphere”.

Using water as a natural filter, the system operates automatically and pollutants are removed thanks to installed sensors and electromagnetic valves coupled into the automatic control system.

Conclusions and outlook

Initial tests conducted in the last quarter of 2012 have proven the suitability of this design in terms of safety, control systems operation and such parameters as heating rate, maximum temperature, vacuum level in the system and gas flow. Previous conclusions clearly show full readiness for technological trials, which will be described along with the theoretical background in the second part of this paper.

Acknowledgements

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References

- [1] Rudolf, R., Friedrich, B., Stopic, S., Anzel, I., Tomic, S. Colic, M (2012): “Cytotoxicity of Gold Nano-particles Prepared by Ultrasonic Spray Pyrolysis”, *Journal of Biomaterials Applications*, 26, 1, 595-612
- [2] Stopić, S., Friedrich, B., Dvorak, P. (2006): Synthesis of nanosized spherical silver powder by ultra-sonic spray pyrolysis, *Metall*, 60, 6, 377-382.
- [3] Bogovic, J., Stopic, S., Friedrich, B. (2011): Nanosized metallic oxide produced by ultrasonic spray pyrolysis method, *Proceeding of EMC 2011, Duesseldorf, June 26-June 29, 2011, Volume 3: Resources efficiency in the non-ferrous metals industry-optimization and improvement*, 1053-1064.
- [4] Gürmen, S., Ebin B., Stopic, S., Friedrich, B (2009): Nanocrystalline spherical iron-nickel (Fe-Ni) alloy particles prepared by ultrasonic spray pyrolysis and hydrogen reduction (USP-HR), *Journal of Alloys and Compounds*, 480, 529-533.