SPRAY PYROLYSIS EQUIPMENT FOR VARIOUS APPLICATIONS
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ABSTRACT

The fabrication of all kinds of industrial products is based on the specific combination between the applied methods, and the conditions of syntheses (temperatures, pressures, flow rates and the chemical compositions of gaseous and liquid fluxes, etc.), resulting on the properties and performance of the obtained products. On the other hand, both the methods and the conditions for synthesis depend on the available equipment, which is able to supply suitable conditions for synthesis via Spray Pyrolysis (SP) and further treatments of the desired product. The present work is an attempt to summarize the basic types of equipment, and conditions for obtaining of products for various applications, via the spray pyrolysis method.

Keywords: Spray pyrolysis, Basic concepts, Synthesis, Deposition, Parameters, Conditions.

INTRODUCTION

The aim of the present work is to summarize the basic constructive elements of the equipment for spray pyrolysis synthesis of powder materials, deposition of thin films, or multilayer systems for various applications. It could be mentioned that basically, the method applied for synthesis predetermines the form of the obtained product. Its properties, as a consequence of the conjunction of its composition, and structure depend on the conditions used for each particular synthesis. The composition of the product depends simultaneously on the composition of the precursor’s solution, the physical processes, and the chemical conversion reactions during the synthesis, as is described in the present work.

METHODS

Synthesis of particles

Systems by direct flame: The performance of this method requires passing of precursor’s flux across a direct flame. By that manner, all chemical (oxidation) and physical (evaporation and pore formation) processes of conversion proceeds in the flame. With a zinc acrylate–methanol–acetic acid solution, the authors [1] have obtained nano-sized particles with crystalline structure and particle size between 10 and 20 nm. The particle size has been controlled by the flow rate and fuel/oxidant ratio. The method can proceed either by supplemental burners, mounted near to the spray nozzle, or by additional feeding of the nozzle by oxidant (air or pure oxygen) and the combustibles. If the spray solution is prepared in an organic solvent, then the latter can serve as a flame fuel, as well.

2.1.2. Synthesis in a high temperature chamber

The chambers are generally thermally insulated boxes or tubes, with electric heaters, which contain recipients for the collection of the powder products, or targets (substrates) for film deposition. If atmospheric air is present in the chamber, and then the thermal decomposition of the precursor’s compounds occurs, accompanied by oxidation of the respective metal. Consequently, always the products are in the form of metal oxides. By application of an ultrasonic nebuliser and a horizontal tubular chamber with three separated temperature zones,
Kozhukharov et al. [2] have obtained a large variety of sub-micronic powders of polymetallic oxides with perovskite structures and even size distribution. Various frequencies of ultrasound nebulising are proposed by different authors, varying from 20 kHz, to 2.5 MHz [3-8]. Additionally, in [3, 6] the authors propose an empirical dependence between the frequency applied, and the droplet size:

\[
D = 0.34 \left( \frac{8 \cdot \pi \cdot \gamma}{\rho \cdot f^2} \right)^{1/3},
\]

where \(D (\mu m \times 10^6)\) is average droplet diameter, \(\gamma\) is the liquid’s surface tension (N m\(^{-1}\)), \(\rho\) is the solution density (kg m\(^{-3}\)), and \(f\) is the ultrasonic frequency (MHz).

When a nozzle is used instead of an ultrasonic nebuliser, the diameter of the spray drops depends on the diameter of the nozzle outlet tip, the surface tension of the respective precursor solution, its viscosity, and the pressure difference before and after the spraying (e.g. inside and outside the nozzle). Alternatively, ultrafine dispersive powders could be produced by swift rise of the temperature inside the chamber, as is recommended in [9]. By this manner, the already formed solid particles undergo further crumbling and splitting, due to mechanical tensions, or phase transitions, occurring at the high temperatures.

Usually, the products of spray pyrolysis synthesis techniques are various metallic oxides, because of the oxidation processes, due either to the simultaneous presence of air and high temperatures, or as consequence of direct combustion of the spray. The latter method for providing high temperatures is described in [1, 10, 11].

Alternatively, the use of chambers with controlled gaseous atmosphere is also reported [12]. Pingali et al. [4] proposed production of metallic silver particles from ultrasonically atomized spray of a silver nitrate solution in water at temperatures above 650°C and below the melting point of silver in a chamber, filled with argon. The particle size achieved was from 20 to 300 nm of diameter.

An alternative approach for modification of the gaseous composition is the usage of volatile anions in the precursor’s solutions, for instance NO\(_2\) or SO\(_4\)^2-. During the pyrolysis, they decompose to metal oxides, and NO\(_2\) or SO\(_4\)\. An interesting example for application of this method is the obtaining of TiO\(_2\) coupled by its partial fluorination for production of photocatalysts [13].

The authors report successful synthesis of F-doped TiO\(_2\) by spray pyrolysis from an aqueous solution of H\(_2\)TiF\(_6\), obtaining either TiOF\(_2\) or TiO\(_2\) with substitutive fluorine atoms inside the titania crystalline lattice. As a result, they obtain a photocatalyst with improved activity.

Kang et al. [14] have used a vertical chamber with an operating temperature from 700°C up to 1200°C, aiming to obtain NaTaO\(_3\) as a photocatalyst, by spraying of a liquid mixture of NaNO\(_3\) and Ta(O\(_2\)C\(_2\)H\(_4\)). Afterwards, they have put the obtained NaTaO\(_3\)-powder into the solution of Ni(NO\(_3\))\(_2\). After evaporation of the water and posterior sintering at 250°C, the authors have obtained a powder consisting of NaTaO\(_3\), impregnated by NiO.

A vertical chamber was used by other researchers for obtaining of water splitting ferrites for solar hydrogen production [15]. The authors have obtained the desired product by spraying of solution of nitrates of Mn, Zn and Fe by an atomizer, mounted at the bottom of the oven. In this case, the obtained Mn\(_{0.7}\)Zn\(_{0.3}\)Fe\(_2\)O\(_4\) was collected in a filter at the upper part of the oven.

While the above mentioned chambers are vertical (Fig. 1(a)), Hirunlabh et al. [12] noticed that the horizontal thermal chambers enable separation of larger and smaller particle’s fractions (Fig. 1(b)). Industrially available horizontal chambers for preparation of oxides as La\(_{0.7}\)Sr\(_{0.3}\)CoO\(_3\) for solid oxide fuel cells (SOFC) applications, is described in detail [16].

The precursor mixtures for spraying can be also colloidal systems, as is proposed by Suh and Suslik [17]. They report successful elaboration of magnetic porous nano-particles spray pyrolysis of a colloidal suspension of Co(CO)\(_8\). The precursor’s mixture has been obtained by stirring of the silica colloid LUDOX SH 40 - 1 ml, styrene-2 ml, ethylene glycol dimethacrylate - 1.6 ml, Azobisisobutyronitrile - 16.4 mg, Co\(_2\)(CO)\(_8\) - 0.15 g and 1,4-dioxane - 30 ml, in 75 ml of aqueous 0.01 M sodium dodecylsufonate in purified water. The ingredients have been mixed and nebulized at 1.7 MHz with N\(_2\) or Ar carrier gas. The obtained product has been collected in bubblers and separated by centrifugation. As a result, the authors have obtained either consolidated spherical submicron particles (at 200°C), or porous nanoparticles (at 700°C). This approach allows further modification of the obtained particles by selective dissolving of the silica cores, resulting in the formation of spherical hollow particles, which can be used as catalyst or drug carriers. In that means, the solubility of SiO\(_2\) powders in diluted
hydrolytic acids and even hot water is investigated at the beginning of XX century [18].

**Synthesis/deposition of layers on various substrates**

Successful elaboration of Yttria Stabilzed Zirconia (YSZ) and YSZ – Pt composite films for SOFC and gas sensors was reported in [19]. The films were produced by multiple spraying of solutions of $\text{Y(NO}_3\text{)}_{3/2} \cdot 6\text{H}_2\text{O}$, $\text{ZrCl}_4$ and $\text{H}_2[\text{PtCl}_6]$ in mixtures of citric acid (CA) and ethylene glycol (EG) on various substrates. The authors have successfully obtained dense and uniform layers, as a result of appropriated thermal cycles of subsequent repetition of spraying and annealing procedures. Nakaruk et al. [20] remark the point out crucial importance of the annealing temperature. Thus, they report that after the spray pyrolysis deposition of 0.5 M Titanium butoxide solution, on quartz substrates at 400°C, the films were composed by a single-phase anatase (with 50nm grains), whereas after annealing at 600°C the crystals grow to 100 nm, changing entirely the optical properties of the respective films. Furthermore, it is underlined in the same paper that the annealing at 800 or 1000°C leads even to phase transition, either to anatase phase (with 100 nm grains), accompanied by rutile agglomerates (700 nm size), or pure rutile films (700 nm grains), respectively. Consequently, the annealing influences both the crystal growth, and the crystal-phase transitions.

In addition, the high temperature posterior treatment can cause a partial fusion of the substrates resulting generally in a remarkable improvement of the film adherence due to diffusion of the film and substrate’s ingredients. This phenomenon was registered by Peshev et al. [21]. After deposition of zirconium oxychloride on silica substrates, followed by annealing at 1100°C, the authors have established formation of $\text{ZrSiO}_4$ by X-ray Photoelectron Spectroscopy (XPS). Obviously, the penetration of Zr into the SiO$_2$ is the consequence of the partial superficial fusion of the silica substrates during the annealing. Detrimental effects caused by the posterior annealing procedure, are also reported in the literature [22]. If it proceeds for prolonged periods, then the extended crystal/grain growth provokes mechanical tension in the deposited layer, resulting in its cracking and detachment from the substrate.

Okuya et al. have deposited a multilayer CuO/TiO$_2$/SnO$_2$ system in order to develop UV-sensors with
maximum intensity at 354 nm [23]. The entire multilayer system has been achieved by the subsequent deposition approach. The process was performed in a chamber for deposition, as shown in Fig. 1(c). The researchers have deposited subsequently five different functional layers, as follows: (1) transparent conductive SnO$_2$; (2) secondary denser layer of SnO$_2$; (3) the photoactive TiO$_2$ layer, (4) layer of CuO; (5) final layer of pure metallic Au.

Sensors for humidity have been developed by spray pyrolysis deposition of Zn$_2$SnO$_4$ [24] and ethanol detectors - by La doped Zn and Sn oxides [25], respectively. In the former article, the authors have established that the composition of the obtained stannate films differs from that of the initial solution sprayed, and also that the simultaneous presence of secondary ZnO or SnO$_2$ phase suppresses the humidity sensing properties of the obtained films. As the main result of the latter study, the authors note that the La doped ZnO films possess superior sensitivity, and the optimal presence of Lanthanum is 3 % at.

An interesting example for usage of a combined system, where horizontal and vertical chambers are simultaneously represented, also can be found in the literature [26]. The authors have successfully deposited SrTiO$_3$ films from Sr and Ti citrates, determining the optimal parameters of deposition process, and the posterior annealing. The authors propose the obtained product to be used in optical recording devices.

Layers of La or Gd doped TiO$_2$ as photocatalysts for environmental applications are proposed, as well [27]. The authors report successful elaboration of La/Gd modified TiO$_2$ on various substrates, like: microscope glass, graphite, metallic Ti, or stainless steel as catalyst carriers. The films were obtained by flame-assisted spray pyrolysis deposition of an initial solution of Ti-isopropoxide and the respective lanthanide nitrates in a medium with CA and EG, nebulised with O$_2$ as a carrier gas. The combustion of the organic substances in the oxygen enriched atmosphere was provided the flame for the pyrolysis process. Again the authors underline that by multiple repetitions of the deposition procedures with appropriated annealing after each cycle, they have achieved easily control of the density, uniformity and thickness of the respective films. The obtaining of La$_2$Ti$_2$O$_7$ layers, by application of similar approach is reported, as well [28].

Other examples for production of lanthanide films by spray pyrolysis can be also found [29, 30]. This method is applicable for hi-tech materials, such as superconductors [31-34], or semiconductors [35, 36].

Fig. 1 represents the basic types of constructions of the equipment for spray pyrolysis.

As can be seen from the figure, the spray nozzle or nebulizer, heat source, and product collector (or substrate for deposition) are the basic operation units of each SP installation, regardless of its construction. Additionally, the pressure necessary for spraying could be provided either by pumping of the precursor solution, or by compressing of the respective carrier gas. The SP systems can be supported by optional gas sources, or even vacuum pumps for control of the gas medium inside the SP chambers. Another possibility is to assemble more than one nozzle. By this manner, the respective nozzles can implant different ingredients in the depositing films when they work simultaneously, or to deposit diffusive functional interlayers with extremal adherence when they work subsequently. In conditions of large scale production, when the respective substrates possess large surface areas, the respective nozzles can be moved by plotter mechanisms, providing scan-printing SP deposition.

**Application of alternative heat sources**

Beside direct flame or heating by electric heaters, application of microwaves or laser beams is also possible. Todorovsky et al. [37] have produced a large variety of metal oxides, such as: Fe$_2$O$_3$, Y$_2$O$_3$, CeO$_2$, La$_2$Ti$_2$O$_7$, LaMnO$_3$, etc., using spray pyrolysis, combined with Nd:YAG solid laser radiation and a magnetic field.

Other investigations using laser beam are described by Starbov et al. [38]. They have also used an excimer laser, for posterior annealing of ZnO layers, deposited on lime soda glass substrates. The authors reported that the posterior procedure had improved significantly the properties of the obtained products as gas sensors.

Other authors [39-43] propose spray pyrolysis assisted by plasma, as a high temperature source. In that case, cooling systems are required for the respective installations, in order to prevent their thermal breakdown. Nevertheless, the temperature distribution inside the chambers is easily controllable, because the plasma arc is composed by ionised particles, and consequently - it can be driven by electric and/or high frequency mag-
netic fields. Another advantage of the employment of high voltage between the sprayer and the substrate for deposition is that the electrostatic charge on the substrate surface enhances the uniformity of the deposited film.

A schematic image of plasma assisted SP equipment is presented in Fig. 2.

The additional needle, illustrated in position b of Fig. 2 enables supplemental diminishing of the spray-droplet size, by both rendering of the higher pressure difference, and decreasing the outlet aperture. The designs of the spray nozzles/nebulizers are the object of patents [44-48], as well.

Another advantage of the plasma heating is the possibility to obtain directly the high temperature crystalline phases, without supplemental annealing. Indeed, Gitzhofer et al. [39] report integrated fabrication of entire solid oxide fuel cells, by subsequent deposition of each functional layer, inside the same SP-chamber, assisted by plasma. Furthermore, in the same article the authors distinguish several basic types of plasma spray pyrolysis, according to the plasma ignition: (i) – Hybrid Plasma Spraying (HyPS) in combination of a direct current and radio frequency; (ii) – Induction Plasma Spraying (IPS); (iii) – Triple Torch Plasma Spraying (TTPS), and (iv) – High-Velocity Low–Pressure Plasma Spraying (HVLPPS) ignited by a direct current.

Concept summary

It can be concluded from the literature review done that the spray pyrolysis enables production of a large variety of products in the form of fine dispersive porous or dense powders or thin mono/multi layer films. With rather simple equipment a large number of parameters of the pyrolysis process, like the size of the spray droplets, chemical composition of the obtained products, their crystal phases, density, etc. can be controlled. Some authors even propose a device which they call “home made” for synthesis and deposition of thin films of CdS and NiO on metallic substrates [49]. The capability for large scale production of ultrafine monofractional powder-like products by relatively simple equipment imposes the SP, as a basic high temperature method for synthesis in the field of the nano-technologies. Nowadays, this capability is the object of intensive R&D activities [1-4, 6-11, 17, 22, 49, 50].

Besides the electric heaters, or the direct combustion of the spray organic ingredients in an air/oxygen environment, the high temperatures necessary for the pyrolysis process could be provided by lasers, arc or induction plasma, etc. This method is basically used for production of ceramic materials, but it enables also production of fine metallic powders [4], and carbon nanotubes [7, 50] with desirable structure and properties. Another important advantage of this method is the possibility to produce uniform and dense films with desirable crystallinity by multiple repetitions of spraying/annealing cycles. Among the most important advantages
of the spray pyrolysis deposition method is the ability to fabricate entire multilayer devices by subsequent deposition of different functional layers, in the same chamber, as is proposed in [23, 39]. Finally, some limitations exist, in relation to the need for temperature control, and the difficulty to obtain low temperature allotropic forms of the respective products. In that instance, the installations for large scale production by SP method need always cooling systems, and precise temperature control.

Nevertheless, the combination between the remarkable simplicity of the equipment required, and the large variety of possible applications of the respective products, as catalysts [1, 13, 14, 22, 27, 28], electronic components [26, 31-36], alternative energy sources, [15, 19, 39, 41, 43], sensors for the industrial automation [19, 24, 25, 38], provides the significant versatility of this method for obtaining of various functional materials and even entire multilayer devices.

CONCLUSIONS

There are several basic types of constructions of equipments for spray pyrolysis:

- According the position of the chamber - horizontal or vertical. The horizontal construction permits size separation of the drops/particles.
- The basic operation units of each SP installation, regardless of its construction, are the spray nozzle or nebulizer, heat source, and product collector or substrate for deposition. Pumps or compressors are also necessary for reaching of the appropriate pressure for spraying.
- The employment of an ultrasonic nebulizer instead of a conventional nozzle enables production of nanomaterials in the form of monodispersive fine powders, with remarkably ease control of the particle size, by variation of the US frequency applied.
- Other possible approaches for diminishing of the particle size of the respective powders are the decrease of the aperture of the nozzle tip and the increase of the pressure difference. Alternatively, the sharp rise of the temperature inside the chamber allows for further splitting of the already formed solid particles.
- According to the heating source, they could be either with electric heaters or by direct flame. The latter approach requires alimentation of the nozzle, simultaneously by the combustible, the precursors and the oxidant. Alternatively, an additional burner should be mounted to the chamber. In the cases of film depositions, the corresponding substrates should be heated. That approach permits cold spraying with posterior heating and drying of the obtained film. It permits a much better control over the structure formation during the course of deposition. The subsequent repetition of the method allows the formation of multilayer systems, which possess combinations of properties. Further improvement of the obtained films could be achieved by posterior annealing. This approach enables even fabrication of multilayer devices by deposition of different functional layers in the same SP chamber. It is the most important advantage of the Spray pyrolysis as a technological method.

The application of alternative high temperature sources, as lasers, or plasma has been investigated, as well.

The combination of the simplicity of the required equipment and the variety of possible applications of the SP products, predetermine its versatility and characterize it as a basic high temperature method of synthesis, reliable for large scale production. Finally, the possibility to perform several processes in the same SP device predetermines the availability for remarkable rise of the production efficiency, and decrease of the technological time.

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REFERENCES

16. accessible via: http://www.sintef.ntnu.no

31. I. Stambolova, K. Konstantinov, D. Kovacheva, M. Khristov, P. Peshev, T. Donchev, Spray pyrolysis deposition of polycrystalline magnesia films and their use as buffer layers in Bi(Pb)-Sr-Ca-Cu-O/MgO/Al$_2$O$_3$ (or glass ceramics) structures, Mater. Lett., 30, 5-6, 1997, 333-337.


34. L. Mancic, O. Milosevic, M. De F. Da Silva Lopez, F. Rizzo, Rapid formation of high Tc phase in Bi-Pb-Sr-Ca-Cu-O system, Physica, C 341-348, 2000, 503-504.


