Chapter 2
History of Flame Spray (FS) Technique

Abstract The flame spray (FS) technique has been practiced in a non-intentional way since the prehistoric age, according to paintings observed in the walls of caves in China. At that time, its principles were not understood, but people had the knowledge to produce the pigments used in the paint by the FS process. The first contemporary reactors for nanoparticles flame synthesis started in the 1940s, by the production of fumed silica. Only in 1971, G.D. Ulrich pioneered the first principles of the FS method. Since this day, several laboratories and companies have developed different apparatus and alternative methods, aiming to obtain materials with improved properties. This is the main driving force for the evolution of the FS process during the last decades, where more materials and equipments are reported in literature.

Abbreviations

FS	Flame spray
NCPDP	Nanocerox Ceramic Powder Development Process
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
XPS	X-ray photoelectron spectroscopy.

In the last years, scientists have been searching a way to improve the properties of several materials, aiming to develop better products for human health, environmental friendly products, electronics, oil and gas industry, steel industry, etc. Since the Richard Feynman's classic talk in December 1959 "There's Plenty of Room at the Bottom," nanomaterials have been arisen as a great opportunity to overcome this problem. According to Feynman, nanotechnology aims to create new materials and develop products and process based on the modern ability to manipulate atoms and molecules. Inside this wide field of nanotechnology and nanomaterials, particles in the nanometric size have been studied in-depth due to their unique physical and chemical properties, which are strongly different from the bulk microstructures. An extensive research activity over the past decade has led to the development of

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several methods for producing nanoscale materials with a wide range of chemical compositions: solgel, combustion solution synthesis, etc. However, a recent technique named flame spray (FS) has arrived as an alternative method to produce nanoparticles.

The technology concerning the FS method is associated to the formation of small particles from a gas or vapor phase in a flame. Consequently, each process used in the past and based in these principles can be described as a FS method. Thus, it is believed that the FS technology has been practiced in a non-intentional way since the prehistoric age, according to paintings observed in the walls of caves in China (Pratsinis 1997). Soot, which can be considered as flame-made particles, has been part of mankind's history. It is observed in drawings on cave walls in the prehistoric period and in the Egyptians, Indians, Greeks, and Chinese culture (Strobel and Pratsinis 2007).

Carbon black is the oldest aerosol that is still manufactured. In short, carbon black was first made in India and Egypt at prehistoric times and was systematically manufactured for pigments in China by pyrolysis of vegetable oils, using the "lampblack" process at about 1500 BC (Pratsinis 2011). Carbon black was also the first commodity to attain industrial significance. It is a pigment formed by 99.5 % of amorphous carbon with different levels of particle sizes with different structures, which justifies its wide range of industrial applications.

Cabot Corporation is the world largest carbon black producer. The Cabot Corporation started when Godfrey Lowell Cabot in 1882 applied for a patent for an apparatus to produce carbon black. In this apparatus to produce carbon black, Godfrey combined his knowledge of pigmentation and chemistry with an understanding of natural gas to become the earlier producer of carbon black. At that time, carbon black was found to use in newspaper and magazine printing inks as well as tires, for example.

The first contemporary reactors for nanoparticles flame synthesis started in the 1940s, by the production of fumed silica. However, only in 1971, G.D. Ulrich reported the first principles of the FS method. Basically, the work of G.D. Ulrich comprised the spraying of silicon tetrachloride ($SiCl_4$) precursor solution in a flame to produce silica as final product (Ulrich 1971).

Silica and titania were the first materials produced by FS synthesis to be patented (Keskinen 2007). TiO_2 is nowdays the largest (by volume and value) ceramic material made in flame aerosol reactors (Pratsinis 2011). For example, Degussa (Evonik Industries), one of the world largest chemical companies, produces flame-made nanoparticles named AEROXIDE® TiO_2 P25, which is a titania photocatalyst that is used widely because of its relatively high levels of activity in many photocatalytic reaction systems.

The discovery and consequently application of a new product (nanoparticles) were the main responsible for the development and research of new aerosol reactors, as for example the use of carbon black to reinforce rubber (Pratsinis 2011). Moreover, the technologies involving the FS process or aerosol manufacturing have been historically developed as a result of the specific necessity for special products. Nowadays, several companies have used the FS technique to produce a wide range of commodities, such as Evonik, DuPont, Kemira, Tioxide, Corning Glass, General Electric, and Nanocerox. For example, in 2003, Degussa started an internal program named Advanced Nanomaterials that led this company to the worldwide leading technology position in the supply of new nanomaterials via gas-phase synthesis as such as FS.

Concerning the wider range of nanomaterials nowadays produced by the FS process, in the last few years, a special attention was given to the doping of nanoparticles, as Pd/TiO_2 (Mekasuwandumrong et al. 2011), Nb/ZnO (Kruefu et al. 2011), and the mixed oxides such as $CoMo/Al_2O_3$ (Høj et al. 2011), Zn_2TiO_4 (Siriwong et al. 2012), CeO_2–$CeAlO_3$ (Aruna et al. 2009), $LiMn_2O_4$, $Li_4Ti_5O_{12}$, and $LiFe_5O_8$ (Ernst et al. 2007) and SnO_2/TiO_2 (Ifeacho et al. 2005). The production of rare earth oxides was also reported, as Lu_2O_3 (Baker et al. 2012). Even biomaterials, for example, hydroxyapatite, one of the most important bioceramic used for bone regeneration purposes in medicine can be produced by the spraying of a precursor solution in a flame (Trommer et al. 2009). However, it is not the intention of this chapter to describe the different materials that can be produced by FS technique. The materials mentioned in this chapter only reinforce how the FS technique has been always in evolution. Moreover, the development of new devices, the use of new flame configurations, theoretical studies of flame synthesis process, and the use of modern tools of analysis (TEM, SEM, XPS) allowed the FS technique to grow up, since the prehistoric carbon black produced in China to novel materials and fields of application.

The use of a flame to obtain several materials has emerging as an important industrial technique and has become recognized across the scientists. The number of researchers as well laboratories that uses the FS has increased in the last years. Some start-up companies were also identified, mainly to develop new spray and flame configurations, and synthesis of novel materials with enhanced properties. One example of a start-up company that produces nanoparticles based in the FS process is the American company Nanocerox. The platform used by Nanocerox is referred to as the Nanocerox Ceramic Powder Development Process (NCPDP) and based upon an exclusive license from the University of Michigan for its patented flame spray pyrolysis process used to produce highly pure, chemically precise, and uniformly sized nanoparticles.

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