Pulsed compression reactor
for nanoparticles manufacturing

Nanoparticles can be produced by different methods such as flame aerosol or plasma processes, sol-gel, etc. Novel pulsed compression reactor seems to be very attractive for a large-scale production of nanoparticles due to high energy efficiency, ability to create unique reaction conditions and process a very broad spectrum of precursors. Therewith unique nanopowders of metals, oxides, carbides, nitrides etc. can be produced.

Particles with a diameter smaller than about 50-100 nm show unusual mechanical, thermo, physical, electric, magnetic and optical properties compared to bulk material with the same chemistry. They can be used to produce unique pigments, fillers for plastics, composites, catalysts, magnetic materials, advanced ceramics etc.

However many potential applications of nanopowders are limited by the lack of large-scale economical production methods. Today the most cost-effective process for production of ultra-fine particles is flame aerosol synthesis. It is employed widely for manufacturing of carbon black, fumed silica, titanium dioxide etc. [1-3].

However there are several grave disadvantages typical of the flame-based synthesis. First of all a feed has to be flammable i.e. to contain a fuel and oxygen. Production of many pure oxygen- or carbon-free metallic and ceramic particles is impossible in flames. Other methods are practicable only for producing research quantities. Plasma-based synthesis, for instance, necessitates a huge amount of electricity to heat up reagents and carrier gas to reaction temperature. In case of very high production volumes (for example 3 millions tones of titanium dioxide worldwide) that results in remarkable energy expenses and high product cost.

However there is much more efficient way to heat reagents - adiabatic compression. It is well known that a compression of gases with no heat loss (adiabatic) is accompanied by a rising of the gas temperatures, an expansion – by a falling. If the compression is rapid enough, the process is close to adiabatic. This type of rapid compression is typical of many technical devices such as high-speed piston engines etc. In case of a very short (<0.01s) duration of the compression-expansion cycle temperatures up to 10,0000 K can be attained [4].

There were successful attempts to use this principle in chemical technology. Amongst them are syntheses of Si and SiC nanoparticles through the pyrolysis induced by the rapid compression of silane in argon and tetrametilsilane in argon-hydrogen mixtures [5, 6].

However, all the attempts to develop an industrial reactor based on rapid compression have been failed.

The free piston pulsed compression reactor outlined here is probably the world’s first reactor of such a type. It could be used for a cost-effective, large-scale production of different nanoparticles.

Reactor concept

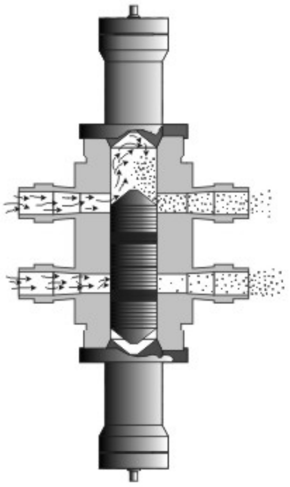

Figure 1. Reactor basic principle

In principle (Fig.1) reactor is a vertically installed cylinder with two covers and inlet and outlet ports for feeding reactants and removing of reaction products. A so-called free (freely reciprocating) piston divides internal volume of the cylinder into two chambers.

The reactor operation is similar to that of a conventional two-stroke engine. The free piston reciprocates as a pendulum swinging between two gas springs compressing in turn a feed gas in both chambers. The reciprocation can be maintained by virtue of a heat release of exothermic chemical reactions (engine-like operation) or by an especially designed pneumatic driving system in the lower cover. In the last case the lower chamber is used as a pneumatic cylinder.

The rapid, almost reversible compressive heating a gaseous or aerosol feed in the chamber generates a dense, hot, homogeneous reactive gas mixture with the temperature typical of plasma chemistry (up to 3000-4000K). Such a mixture is an ideal medium for an almost instantaneous decomposition and evaporation of precursors. The following expansion is accompanied by very rapid quenching (up to 107 °C/s) of the hot reaction mixture. That resulted in a formation of clusters, which further grow to nanoparticles by a surface growth, coagulation and coalescence. When the piston opens inlet and outlet ports, the aerosol produced is forced out by the coming feedstock and then the cycle repeats itself.

Duration of the extremely high temperatures does not exceed 10-3 s. preventing a significant heat exchange between the hot, compressed media and relatively cold walls of the reactor. This provides both almost isentropic compression-expansion cycle and the feasibility of handling the temperatures that go far beyond the limits determined by heat and hot corrosion resistances of any structural materials.

In contrary to engines, the piston reciprocates without contact with the cylinder. Such a self-alignment of the piston in the cylinder is known as gas lubrication (gas bearing). A leakage of a compressed media between the piston and cylinder is insignificant due to very small clearance (so-called labyrinth sealing). The contactless operation permits the reciprocation of the piston with a very high frequency (up to several hundred Hz).

The reactor can handle two operation modes:

1. **High-exothermic process in the upper chamber**. In this case the reciprocation of the piston is maintained at the expense of heat release of a high-exothermic reaction. If the heat release is not high enough, an additional energy can be generated by combustion of an appropriate fuel – hydrocarbons, ammonia etc. This regime could be used for producing a broad spectrum of nanoparticles (oxides, metals, carbon black etc.) which normally are manufactured by flame-based technologies. A possible example is production of titanium oxide:

   $TiCl_4 + O_2 – TiO_2 + 2Cl2$

   The method could be used to produce complex oxides as well by pyrolysis of mixtures of precursors.

   Synthesis of fullerene-like species also seems to be possible as this takes place in diesel engines [7].

   Metal particles also might be produced by pyrolysis of some metal salt precursors such as acetate, nitrate etc just as in case of flame-based technology [8-10]. The feed could be in form of finely dispersed sub-micrometer liquid droplets of aqueous solutions (aerosols) generated by ultrasonic or electrostatic aerosol generators etc. During the compression and the following combustion the solvent is rapidly evaporated and precursors atomized in a carrier gas undergo a subsequent decomposition and chemical reaction.

In spite of presence of oxygen the reactor might produce non-oxide ceramic powders as well because rich hydrocarbon-oxygen flames create a reduction atmosphere containing CO and H_2. A reducing potential of atmosphere generated by incomplete combustion is sufficient to prevent oxidation of many metal particles.

2. **Low-exothermic or endothermic processes in the upper chamber**. In this case the heat release is not adequate to provide the reciprocation. Then the reciprocation is maintained by the pneumatic driving system. This regime can be used for manufacturing of very pure, oxygen-free metallic and ceramic nanoparticles by means of pyrolysis of a number of precursors such as metal carbonyls, hydrides, halides, organometallic compounds etc.:

$$\mathbf{Fe(CO)_5 \rightarrow Fe + 5CO}$$

$$\mathbf{TiI_4 \rightarrow Ti + 2I_2}$$

$$\mathbf{3SiCl_2H_2 + 10NH_3 \rightarrow Si_3N_4 + 6NH_4Cl + 6H_2}$$

$$\mathbf{TiCl_4 + BCl_3 + 5H_2 \rightarrow TiB_2 + 10HCl}$$

Actually all the precursors typical of chemical transport reactions can be used as a feedstock of the reactor as well.

Development of the reactor

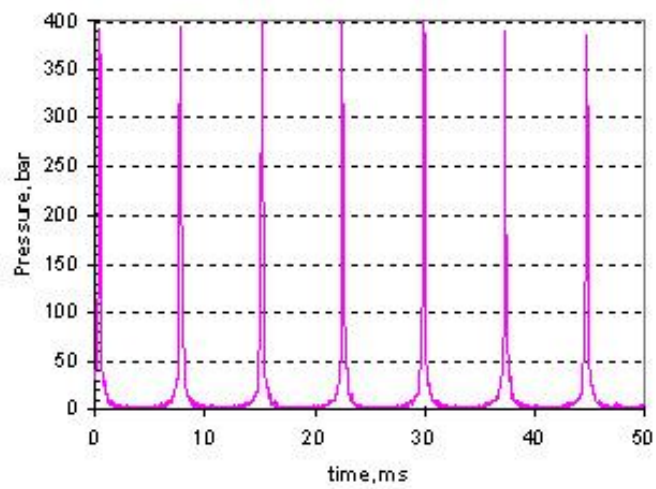

Figure 2. Pressure change in a reactor during continuous production of synthesis gas by partial oxidation of propane with air: air/fuel

Since 1996 eight reactors of different design and dimensions and many pistons of various materials, dimensions and shapes were manufactured and studied. The inner diameter of the reactors was 60 mm. Also a pilot plant for testing of the reactors was built. The main goal was production of synthesis gas (mixture of CO and H_2) and hydrogen.

The reactors demonstrated unique performance [11-17] e.g.:

Compression ratio up to 45.

Maximum compression temperature of inert gases compressed from ambient temperature corresponding to this compression ratio is about 3000°K, for air – of about 1300°K. After preheating up to 200^0C the final compression temperature of inert gases can reach 4500^o K, air – $2000\ ^o$ K.

Frequency of the piston reciprocation – up to 200 Hz.

Such a frequency corresponds to volume throughput in range of 10^7 h-1. The experiments on combustion of ultra-lean and ultra-rich methane-, propane-, hexane-, and ethyl ether-air mixtures were performed to demonstrate a feasibility of the reactor operation in a broadest concentration ranges (far beyond the inflammability range).

Figure 2 shows an example of the pressure change in the single chamber reactor during partial oxidation of propane. In particular, stable operation of the reactors was observed during combustion of propane with air at concentration of propane less than 0.5 and more than 20 vol %. Combustion of so lean and so rich mixtures is impossible with other types of equipment. Combustion of the ultra-rich mixtures was resulted in production of carbonaceous particles.

Figure 2 shows some of the remarkable capabilities of the reactor. The extreme temperatures exist for only very short periods (~ 0.1 ms). As a result, whereas the reaction temperature is 3000^0 K, any desired temperature of the reactor walls can be maintained.

Advantages of the novel reactor concept

Compared to flame-assisted synthesis, it shows much higher temperatures and the ability to combust ultra-rich and ultra-lean fuel-air mixtures which normally are far beyond flammability limits. That makes it possible to produce oxygen-free metal and ceramic particles. In contrary to plasma-assisted technologies the reactor generates very homogeneous mixtures and keeps a desirable reaction temperature without a contamination of products by a material of electrodes.

The rapid decreasing temperatures and concentrations of reactants during the expansion can stop rapidly growth of particles and make them uniform. Such an extremely rapid quenching makes it possible producing amorphous nanoparticles (glasses) with unique magnetic, mechanical and catalytic properties. But most important of all is that the quenching by the adiabatic expansion recovers energy spent on heating in contrary to all conventional quenching techniques (critical flow nozzle, mixing with a cold gas etc). Energy spent for the compressive heating is used directly for the compression in next cycle involving the highest possible energy efficiency. That could make a large-scale production of many nanopowders economical.

Owing to such an unique cycle the reactor can process extremely diluted mixtures to avoid an aggregation of nanoparticles produced. In case of the flame-assisted or plasma-based technologies such a dilution is uneconomical due to unacceptably high expenses of energy (fuel, electricity) for the heating of a ballast carrier gas.

Very high reaction rates and high frequencies of the piston oscillation (100 – 400 Hz) allow very high space velocities, i.e. (GHSV~ 107 h-1) i.e. three-four orders of magnitude higher than space velocities in the conventional chemical reactors. As a result reactor volume will be 1000 – 10000 times smaller than one of conventional reactors.

In spite of extreme reaction temperatures and pressures the reactor is inherently safe due to very small inventory. The volume of the hot compressed gas in the largest realistic reactor will be as less as 1 liter.

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