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Article

High-Energy-Low-Temperature Technologies for the Synthesis of Nanoparticles: Microwaves and High Pressure

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Abstract: Microwave Solvothermal Synthesis (MSS) is a chemical technology, where apart from possible effects of microwaves on the chemical reaction paths, microwave heating allows the precise planning of a time-temperature schedule, as well as to achieve high super-saturation of the reagents uniformly in the reactor vessel. Thus, MSS is suitable for production of nanoparticles with small grain size distribution and a high degree of crystallinity. A further advantage of the technology is a much lower synthesis temperature than for gas phase, plasma or sol-gel technologies. New reactors have been developed to exploit these advantages of the MSS technology of nanoparticles synthesis and to scale up the production rate. Reactor design and realization has been shown to be decisive and critical for the control of the MSS technology. Examples of oxidic and phosphatic nanoparticles synthesis have been reported.

Keywords: microwave solvothermal synthesis; microwave hydrothermal synthesis nanoparticles; microwave reactors; particle size distribution

1. Introduction

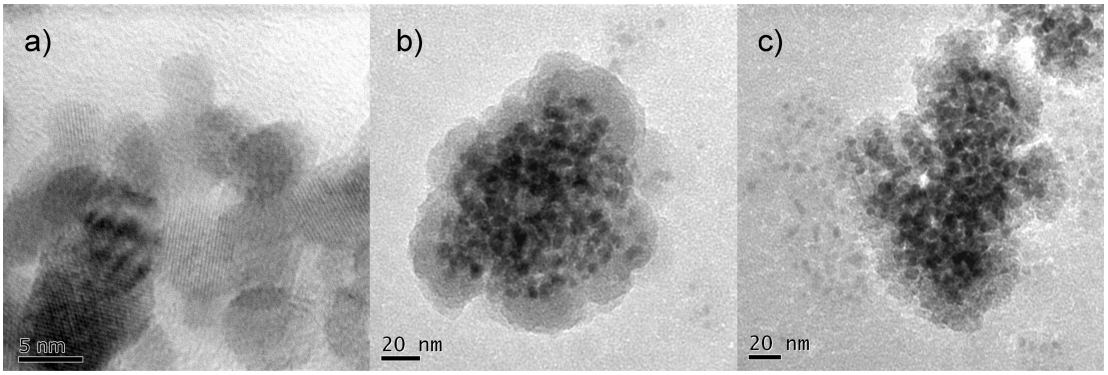
The interest in nanoparticles (NPs) comes from a change of properties in materials when the size of matter becomes less than a critical value, which is usually below 100 nm, and which depends on the physical or chemical property of interest [1]. A large market for NPs, particularly oxide NPs, has already developed [2]. NPs can be considered a valuable additive for different classes of materials [3]. They can also form building blocks for hierarchical structures or for organised nanostructures (nano-architectonics) [1]. Major interest is in controlling the stoichiometry, chemical and phase composition of NPs, chemical gradients at the nano-scale (e.g., surface segregation), size distribution, shape, thickness of the surface layer, and its chemical composition. A challenging issue is to avoid agglomeration of NPs into clusters, which a typical size is from 100 nm to several microns, because in such a case not always can the specific nano-effects be exploited (e.g., optical transparency of colloidal suspensions of NPs). These requirements can be fulfilled only if there is a correlation between the synthesis parameters and the NPs properties, and the reactors used for their synthesis allow precise control the reaction conditions and ensure their optimum values. An important group of such reactors are these that use microwave energy to carry out the solvothermal synthesis (Microwave Solvothermal Synthesis, MSS). Their key advantage is the ability to heat liquids without large thermal gradients and with precisely controlled time schedules [4]. Microwave hydro or solvo-thermal synthesis of materials is a well-established wet chemical process [5–7]. A comprehensive review of microwave technology in application in nanoparticles synthesis was published recently [8]. In this paper, we shortly review some recent developments in design of MSS reactors and the resulting progress in the MSS technology.

2. Advantages of the MSS Technology

There is a large range of methods to carry out nano-particles synthesis, and all of them have some advantages and disadvantages. Wet chemical synthesis, including precipitation or sol-gel methods, is widely diffused. Additionally, these methods seem quite appropriate for low-cost production, and also for production of alloyed or stoichiometric NPs. However, a basic requirement for nanoparticles, especially oxide nanoparticles, is that their synthesis reaction is fully completed. If that is not the case, a layer of hydroxides or other precursors may be present, which negatively affect the nanoparticles properties. Both for the sol-gel or solvothermal synthesis this is achieved by raising the reaction temperature above certain level.

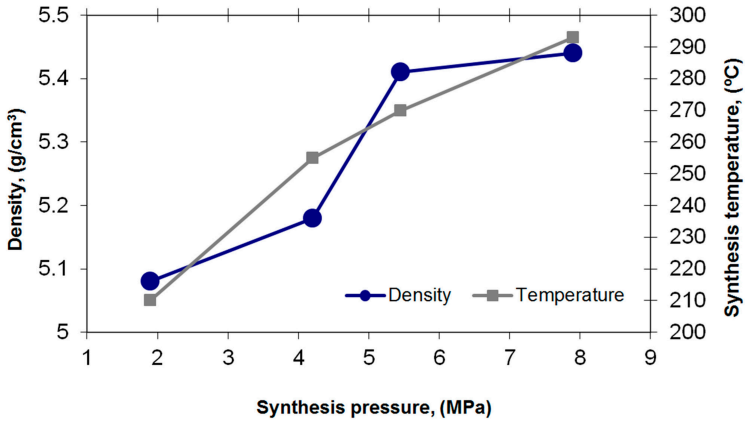
If the synthesis temperature is too low, part of the material remains in the amorphous form of hydroxides, no matter the reaction time. The surface layer of imperfectly crystallised nanoparticles (Figure 1) inevitably leads to a decrease of their density, deteriorating optical properties, or leading to poor dispersion capacity [9].

Figure 1. Examples of nano-sized zirconia particles differing in the degree of crystallinity: (**a**) fully crystallized ZrO_2/calcined 400 °C, 40 min, in air; (**b**) partially crystallized ZrO_2-Eu^{3+} 8 wt% doped, short and (**c**) long heating treatments (MSS).



In a solvothermal environment, high temperatures correspond to high pressures, as illustrated in Figure 2, which illustrates the effect of synthesis temperature and pressure on the density of ZrO_2 NPs [10]. Thus, the hydrothermal or solvothermal synthesis may permit to obtain non aggregated NPs and reduce the treatment temperature, which by ("rule of thumb") is about 50% (measured in °C) with respect to calcination temperature.

Figure 2. Effect of synthesis pressure on the density of zirconia nanoparticles produced in hydrothermal process [10]. At the pressure of 5.5 MPa, corresponding to 270 °C, the particles were transformed from non-fully reacted to fully reacted.

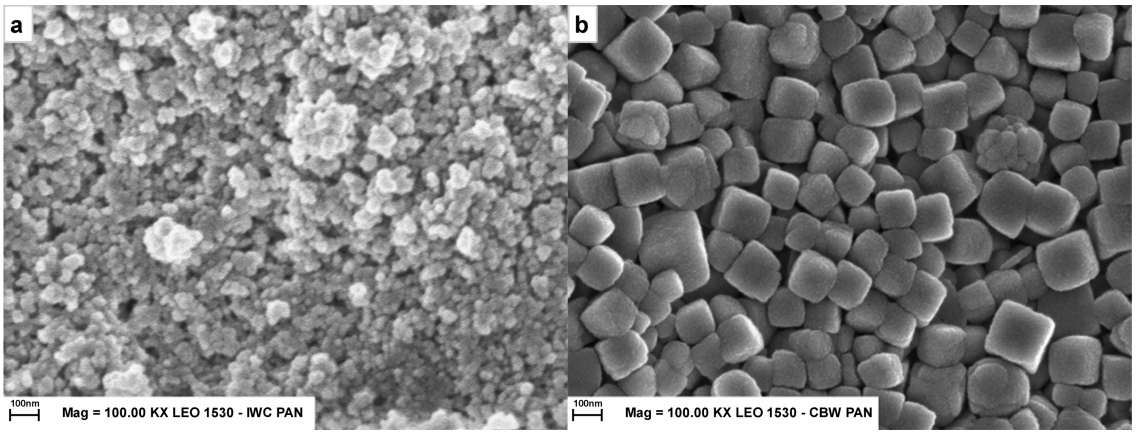


In ref. [9] this situation is further discussed. It is shown that the zirconia nanoparticles are coated with a monolayer of hydroxide even after high temperature calcination: this skin layer is an inherent part of the particle. It causes the nanoparticles' density to be lower than the density of bulk materials, especially for particle sizes less than 50 nm. However, if the synthesis pressure or temperature is too low, the unreacted part of the nanoparticle is thicker than one monolayer, and the density of NPs is not optimal.

Crystallisation of NPs of pure oxides, mixed oxides, phosphates, carbonates and other inorganic compounds produced at low temperatures (*i.e.*, below 100 °C) as a rule, requires a second reaction step: annealing. For yttrium-aluminium garnet, $Y_3Al_5O_{12}$ or YAG, nanoparticles, the annealing temperature is above 1000 °C [11], for ZrO_2, about 500 °C, and for ZnO, about 200 °C. This calcination process

leads to nano-particles sintering and aggregation. Such a two-step synthesis route can be substituted with a single step, a solvo or hydrothermal synthesis, which is carried out at temperatures much lower than calcinations [12]. As an example, in Figure 3 we show YAG NPs produced in a solvothermal process at 450 °C [13] and in a sol-gel process (followed by annealing at 1100 °C [11]). The sol-gel particles form hard aggregates of NPs, while those prepared with solvothermal process are not strongly bonded to each other.

Figure 3. Comparison of aggregation for nano-YAG powder produced using (**a**) the precipitation method followed by calcination at 1100 °C and (**b**) solvothermal process at 450 °C.



Additionally, it is not only the maximum possible crystallinity level that is required, but also a narrow size distribution and controlled dimension. To achieve this goal, the solution of reagents needs to be uniformly heated at a high rate until a given degree of oversaturation is achieved, and then the heating should be stopped to avoid grain growth. This procedure should lead to uniform nucleation of NPs in the whole volume of the liquid [4]. An extension of the heating time will lead to Ostwald ripening and widening of the particle size dispersion.

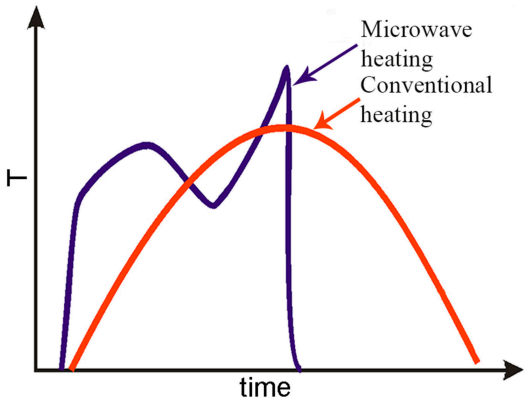
How to achieve such a rapid overheating in a liquid? Conventional heating methods will inevitably lead to a situation where the hot heater contacts a cold liquid; hence, the reactive liquid will experience strong temperature gradients. A possible method is to heat a small volume of a liquid flowing through a narrow tube. This is the so-called continuous solvothermal or hydrothermal synthesis [11,13]. Another possible route is to use electromagnetic radiation, which penetrates deep enough in the reaction vessel, so that the heating rate is much more uniform than during conventional synthesis. This approach permits also the fast heating of the total volume of liquid due to turbulences caused by local microwave energy "hot spots". The fundamental difference of the two processes is that in the continuous process it is difficult to control the time the NPs spend in the reaction zone, while during the MSS process, time of reaction can be precisely controlled. So, the use of microwave energy as a heat source is advantageous if control of reaction time is needed.

Application of MW energy in chemical synthesis is well established [14,15]. In the case of solvothermal synthesis it allows for additional control of the synthesis process, besides fast heating solely. The subject was reviewed recently in the paper [16] and in the monograph edited by Horikoshi and Serperone [8]. Figure 4 shows schematically further opportunities MW heating offers during NPs

synthesis. In case of conventional heating, the thermal inertial of the system limits the heating rate and cooling rate. In the case of MW heating, one can not only rapidly heat, but can also change the temperature during the process, and at the end also rapidly cool the product, since the vessel walls temperature need not to be coupled with the temperature of the vessel content.

Further, it may be advantageous to have a controlled temperature gradient by focussing the MW energy in a particular part of the vessel, and further shorten the time the nucleated NP spend in the high temperature zone. As it is seen, the details of the microwave heating process strongly depend on the MW reactor design, which sometimes makes it difficult to compare results from various research groups. A thorough review of various reactors for MW synthesis of nanoparticles can be found in [8].

Figure 4. Schematic presentation of the thermal microwave effects as variation of temperature in time.



There is also the wide area of research concerning specific MW effects, where it is expected that in a strong electromagnetic field the course of the chemical reactions is changed [17], or where MW interact with individual NPs influencing their nucleation and growth process. This subject is outside the scope of the present paper, and more information can be found in [18].

In the MW hydrothermal process, the strong variation of the dielectric properties of water with temperature has to be accounted for, since they affect MW absorption, reactants' solubility and supersaturation. It is well known that water can easily dissolve ionic compounds, typically the salts of metals used in the preparation of oxidic NPs. It is also known that its polarity decreases with increasing temperature and the dielectric constant may become very close to that of unpolar solvents in near supercritical conditions [19]. Such a decrease in polarity is accompanied by the sudden commencement of supersaturation, which leads to nuclei formation, the first step for NPs' preparation. The supersaturation in water/aqueous solutions is very well known also in common hydrothermal treatment, but the uniformity of temperature profile, which can be reached in thick walled reaction vessels, is a peculiar feature in MW heating.

The above advantages of the MSS process are called MW thermal effects [20], since they result from thermal schedules that are impossible to achieve using other heating methods.

A major limitation when comparing MW synthesis in the liquid phase and conventional heating is that it is quite difficult or even impossible to carry out two syntheses, one using MW and the other without, and follow the same temperature-time schedule. Thus, even if the results of the two processes are different, the reason of this difference could be either a divergence in the heating process or a real

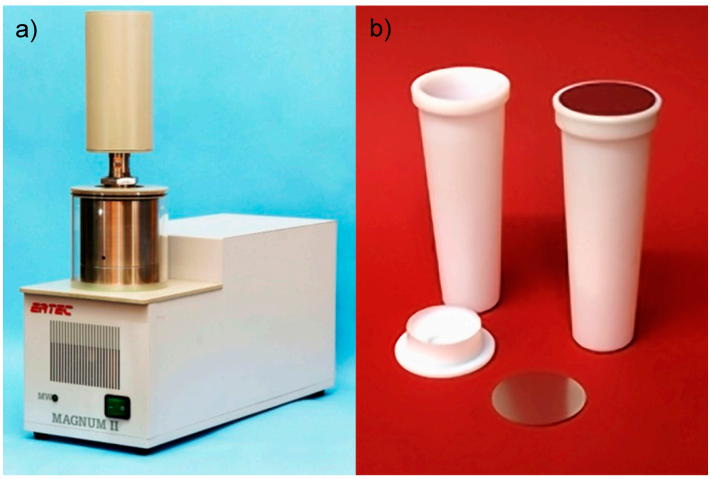
modification of the reaction path. A thorough review of application of MW in NPs' synthesis is given in the already mentioned monograph [8].

In the following sections, we will give several examples of MW reactors used for NPs synthesis and will show two examples where MSS of nanoparticles shows a clear advantage possibly due to MW indirect heating application.

3. Reactors for MSS Synthesis Developed at the Institute of High Pressure Physics—IHPP PAS

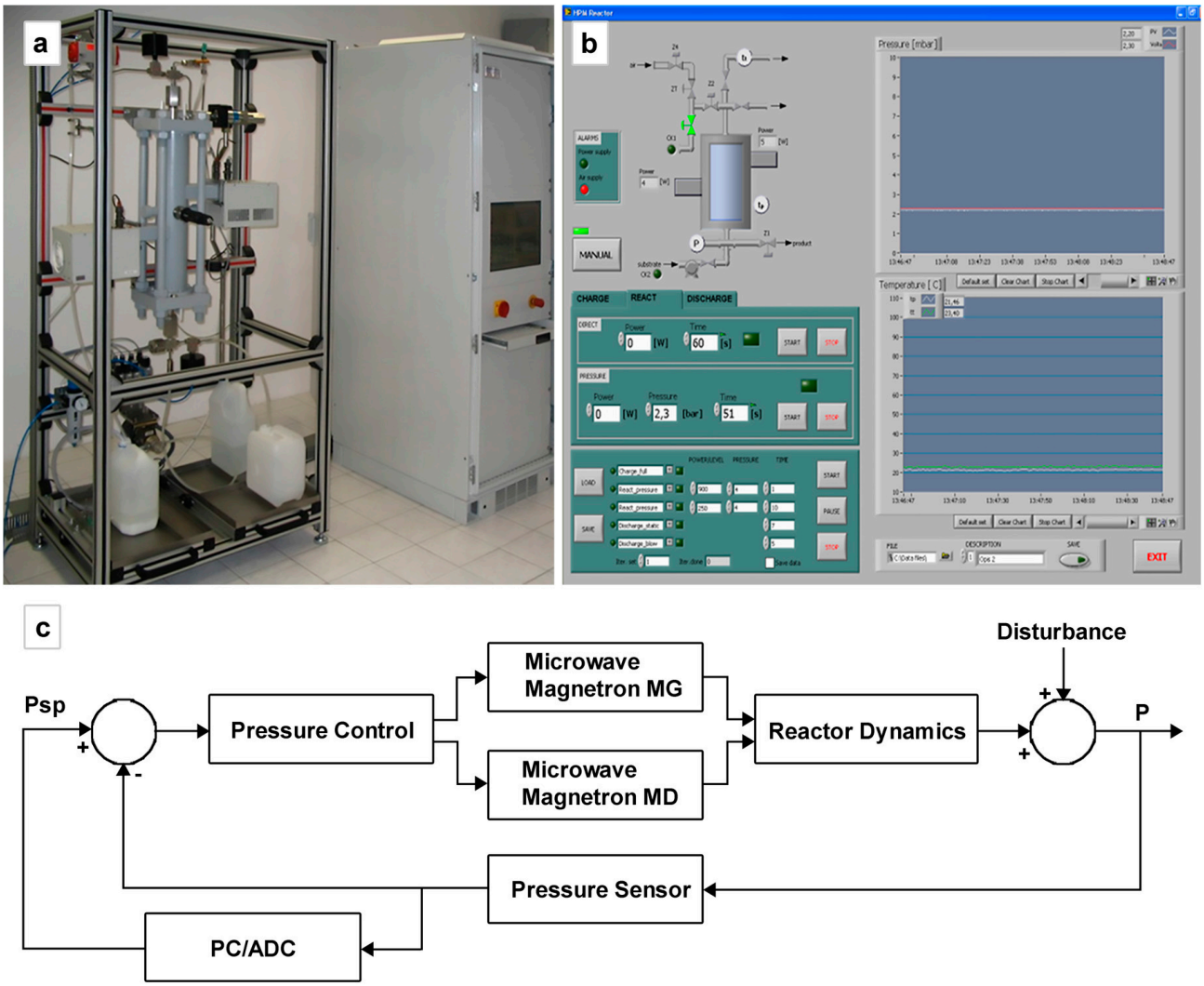
The MSS adventure at the Institute of High Pressure Physics, IHHP, started with the application of a simple MW reactor developed by the company Ertec-Poland, "Magnum II" (Figure 5). A Teflon® vessel with a volume of 10 mL is enclosed in a pressure vessel made of steel. A MW antenna focuses the energy at the bottom of the Teflon® vessel. An energy density of about 5 W/mL is achieved at the bottom of the vessel, permitting to raise the temperature at a rate of approximately 1 K/s. The maximum temperature is 300 °C for short operation, and the maximum pressure is 10 MPa. All parameters—pressure and temperature—are controlled. The Teflon® vessel can be changed for each reaction, which is essential if high purity of the product (no cross contamination) is required.

Figure 5. (**a**) The reactor Magnum II [21] with its; (**b**) Teflon® vessels with a recommended amount of nanoparticles produced in single batch process of about 1.5 grams.



The two reactors shown below (Figures 6 and 7) have been developed at IHPP in collaboration with the company Ertec—Poland and the Institute of Sustainable Technology in Radom, Poland. The reactor MSS-1 is a stop-flow reactor, automatically operating, with a chamber of volume 250 mL, maximum operating pressure 4 MPa and temperature 240 °C (Figure 6). The reaction chamber is a Teflon® tube, 3 cm in diameter. MW energy is supplied by means of two magnetrons with 1 kW output power. The magnetrons are placed at different levels in the chamber, opposite to each other. The temperature of the PTFE chamber is measured with the use of a pyrometer (TXP7, Raytek, Santa Cruz, CA, USA), which is placed between the magnetrons. The pressure is measured with a pressure sensor with a capillary and a separation membrane (SEN-3291, Kobold, Pittsburgh, PA, USA). The circulator prevents reflected power damaging the magnetrons. The use of two magnetrons permits a uniform field distribution, but on demand one can use only one magnetron, and achieve a temperature gradient and/or microwave stirring effect.

Figure 6. (**a**) The MSS-1 reactor. Stop-flow reactor, automatically operating, with a chamber of volume 250 mL, maximum operating pressure 4 MPa and temperature 240 °C; (**b**) The control panel; (**c**) Schematic presentation of the control system. Psp is the pressure set point. Magnetron MG/MD means the upper and lower magnetron, respectively.

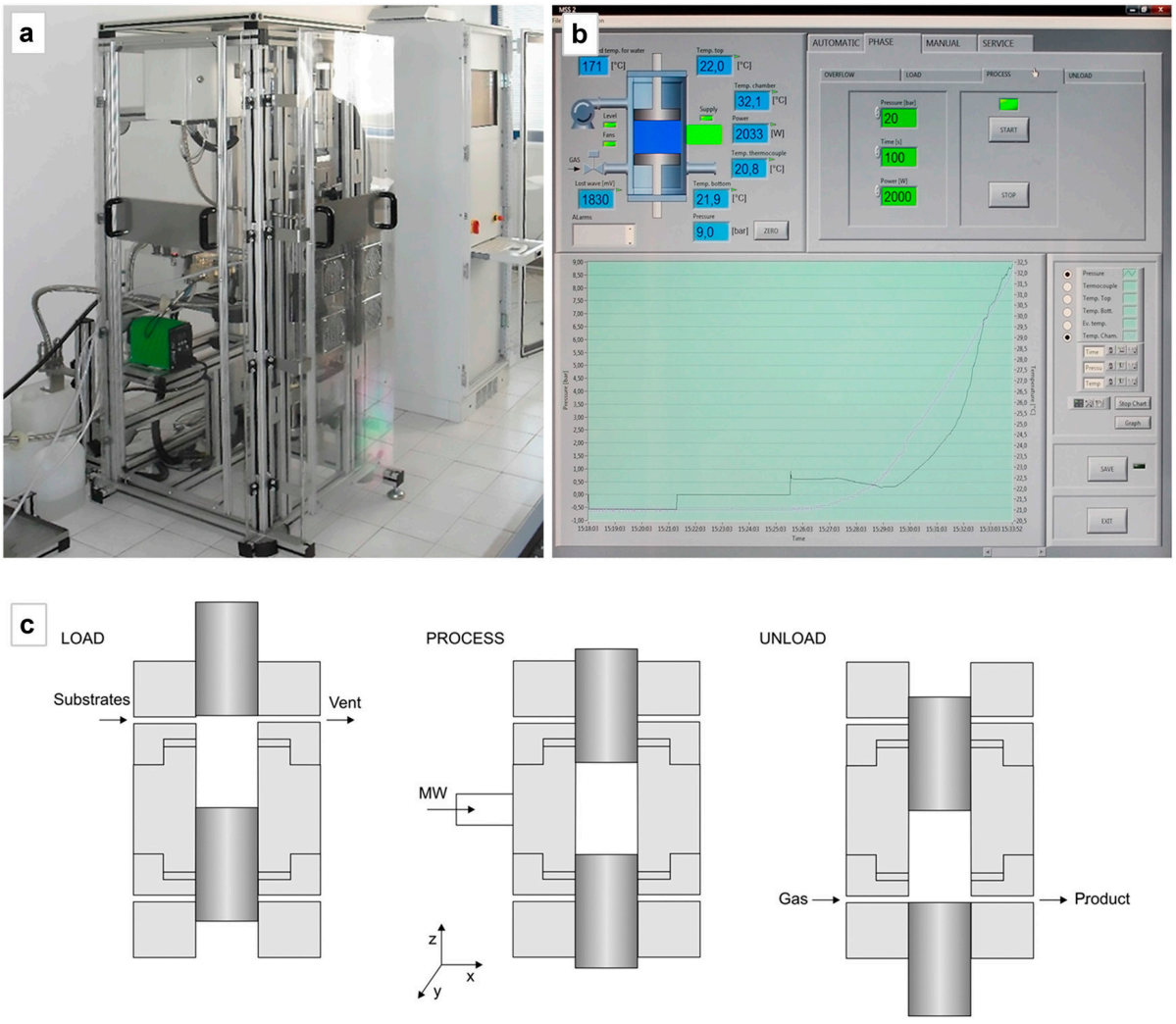


An advanced control system allows for precise control of temperature, pressure, and the measurement of the reflected power. The control system of the device has two layers. The first one (Figure 6b) is the layer of local regulation systems. The more important of the two is the process pressure regulator, in which hysteresis controlling is used, and ensures that the maximum speed of the batch pressure growth is maintained. The dynamics of the process is changeable. It depends mainly on the volume of the batch, its dielectric properties (temperature-related), and the level of the supplied microwave power. The hysteresis controller compensates for the changes in the dynamics at the level of pulsations, which is acceptable for the process. The second layer of the control system (Figure 6c) concerns the superior control, whose objective is to set and monitor the process parameters, monitor the condition the device is in, and to record and read process data. The monitoring of pressure changes is much better due to the application of a quicker (than in the case of the controller in the sampling regulation layer) signal from the pressure sensor. The additional card of analogue to digital converter (ADC), (PCIe-6320, National Instruments), measures pressure with sampling speed 200,000 samplings/s. Such a high sampling speed ensures better

analysis of the course of the process, particularly in the case of sudden pressure changes. The high-pressure valves and the system for product unload enable the chamber to be unloaded at any time during the process. Quick cooling of the product ejected from the reactor is another significant advantage.

MSS-2 is a batch reactor (Figure 7). The pressure of reaction is up to 6 MPa, which is obtained through heating of the batch. However, operation at higher pressure (up to 10 MPa), obtained with the application of the suitable dosing pump or the external source of compressed air, is also possible. The allowed temperature of continuous operation is 270 °C. The capacity of the chamber is 410 mL. A unique structure of a process chamber, uncommon for other solutions of this type, was applied. The structure is closed on both sides with moveable plungers, which in consecutive stages of the process position the batch at the level of load slots of the microwave waveguide and chamber unload slots.

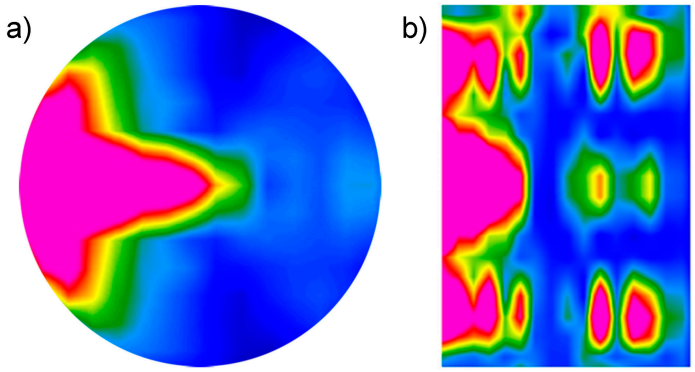
Figure 7. The MSS-2 batch reactor. (**a**) MSS2 reactor general view; (**b**) Control panel and a process diagram; (**c**) Schematic presentation of the reactor operation: loading, processing, unloading.



All the elements that are in contact with the substrate and the product are made of chemically resistant materials—PTFE (connection lines, head of the dosing pump, the middle part of the process chamber, seals) and Al_2O_3 ceramics (plungers, the top and bottom part of the process chamber). The reactor is cooled down with the forced airflow [22].

The dimensions of the chamber were defined with the use of computer simulations (commercial software: QuickWave, QWED, Warsaw, Poland), so that the best adjustment of the chamber to the microwave generation path could be achieved, leakage of microwaves at the ends of the plungers prevented, and a homogenous arrangement of the electromagnetic field is ensured (Figure 8).

Figure 8. Distribution of average bulk density of power losses within MSS-2 reactor filled with water in the *xy* plane (**a**), and in (**b**) the *xy* section. Pink area shows more intense losses.

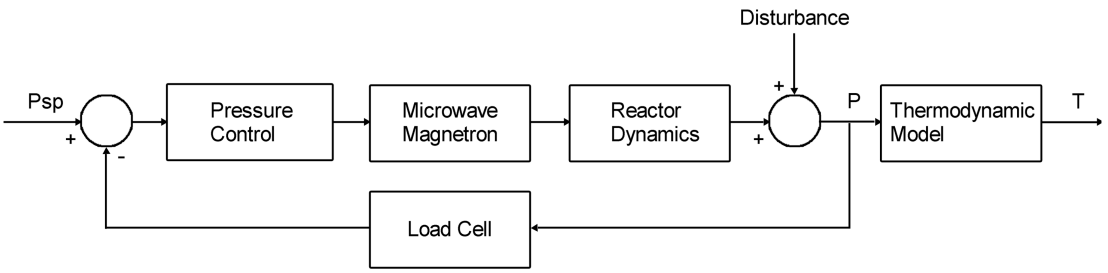


The microwave track of the device includes a generator with a 3 kW magnetron. The track is also equipped with two reeds located in the waveguide connecting the circulator with the process chamber, which—together with a system for the measurement of reflected power—allows for the system to be adjusted at the time of the process. The main tasks realised in the process control system include:

- the regulation of process parameters;
- the superior control over the processes;
- the monitoring and record of the processes;
- the control over the security and emergency states.

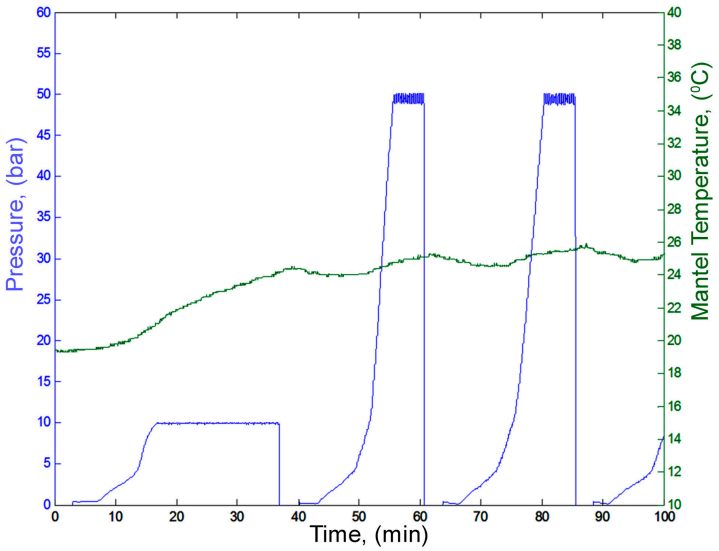
For the regulation of pressure (Figures 9 and 10), due to the fact that the maximum speed of the pressure growth is required, a hysteresis controller, like in the case of the MSS-1 reactor, was applied.

Figure 9. Block diagram of pressure P regulation system and process temperature T determination.



The superior process control is performed according to the PN-EN 61512 norm for the control of batch processes. In this control, the process takes place automatically with the use of a procedure (technological recipe) for single process phases, which is the input for the control PC. The process is divided into four phases: (1) chamber load; (2) process execution; (3) chamber unload; (4) chamber overflow.

Figure 10. Pressure in the chamber and average temperature from outside chamber, batch—deionised water 350 mL.



The main feature of the reactor is its high efficiency. The original architecture of the reactor allows for full automation of the process and the procurement of nanopowders in a significantly greater scale than in the case of the application of laboratory equipment. The device radically speeds up the entire process and makes it possible to obtain products measured in litres, not as in the case of laboratory apparatus, millilitres only. A significant advantage of the reactor concerns the high purity of the reaction process, which is obtained thanks to the application of chemically neutral materials, and low sensitivity to substrates of high density, including suspensions with sedimentation tendencies. The MSS-2 reactor has a built-in system for the measurement of reflected power of microwave radiation. This enables the monitoring of changes in dielectric properties of reagents at the time of the process and helps to determine the dependencies between the absorption of the radiation and the state of reaction, and the on-line adjustment of the energy of the process chamber and the microwave generator. The control system enables automatic execution of processes with consideration of the aspect of the operator and environment safety, and makes it possible for the device to be easily included in a complex technological line.

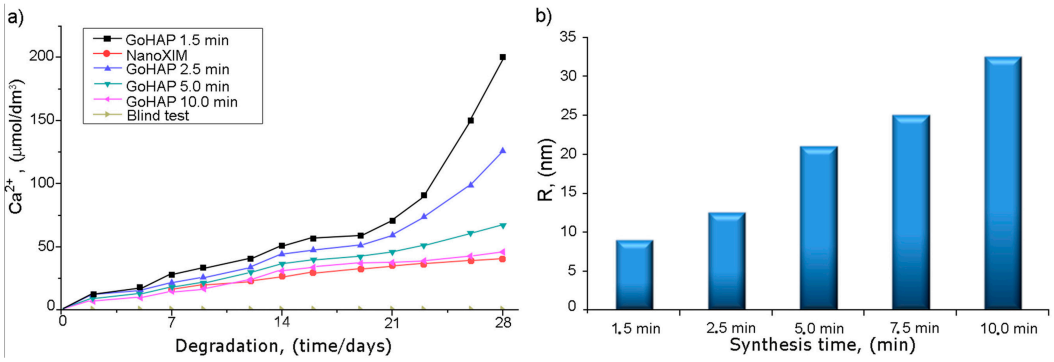
4. Examples of MSS Synthesis of NPs

4.1. Synthesis of Nano-Hydroxyapatite

Nanoparticles of hydroxyapatite, HAP ($Ca_5(PO_4)_3(OH)$) are extensively used in regenerative medicine, e.g., for enhancing bone regrowth, or to improve adhesion of implants to bone. For the application as bone regrowth scaffold, it is required that the material is resorbable, and the natural one gradually replaces the artificial bone made from NPs. However, the HAP particles available on the market are usually not sufficiently resorbable. It is known that MW hydrothermal synthesis can be used for production of high purity HAP [23]. High purity of the product is possible, because the reagents are closed in a vessel made form chemically inert material, and do not contact any heating elements. We explored the effect of the additional variable possible during MSS, namely, precise control of the reaction time. We carried out HAP NPs synthesis using the Magnum II reactor (Figure 5). The details of the

process are described in the papers [24,25]. The prepared solution of calcium and phosphate ions was heated with maximum power until a temperature of 110 °C was achieved. The reaction time varied from 90 s–10 min. In Figure 11a, the resorbtion rate of the nanoparticles is shown. GoHAP is the nanopowder produced using the MSS method, in 1.5; 2.5; 5.0; and 10 min. NanoXim is a reference nano HAP available on the market [26]. The determination of material solubility was performed according to norm ISO 10993-14: biological evaluation of medical devices—identification and quantification of degradation products from ceramics. On the vertical axis it is indicated the concentration of Ca^{2+} ions/dm^3, which is an indication of the dissolution degree of the HAP nanoparticles. Further, the resorbtion rate in a standard test depends on the synthesis time as well (Figure 11): for 10 min synthesis time, it approaches the dissolution time of a commercially available HAP. The particle size distribution was measured using Transmission Electron Microscopy. It is seen that the particle size and distribution depends on the synthesis time (Figure 11b). Thus, application of MW technology permitted to obtain HAP NPs whose resorbtion rate is tuned according to doctors' needs. The material is tested as a coating for bone regrowth scaffolds [27]. This was possible because of the process time control, with precision of a few seconds, is available for the MSS technology.

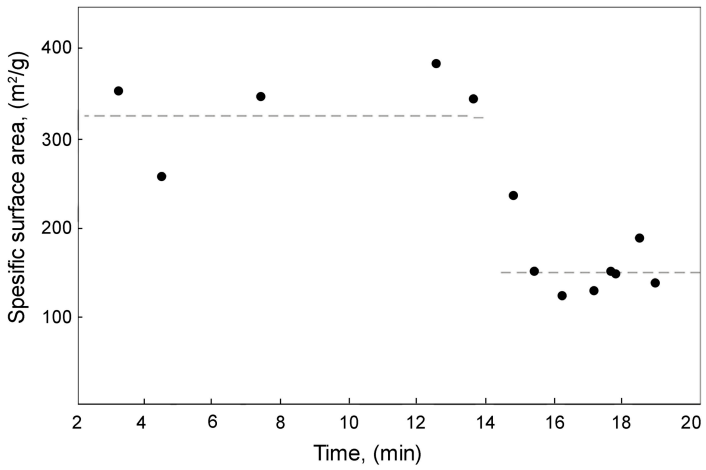
Figure 11. (**a**) Size/time effect on bio-degradability of HAP nanoparticles produced in the Magnum II reactor [24]; (**b**) Grain size, as a function of synthesis [24].



4.2. Synthesis of Nano-ZrO_2

Synthesis of nanosized ZrO_2 using microwave reactors is well known [28]. However, MSS technology offers and additional advantage for the process control, namely: measurement of reflected power. We carried out ZrO_2 synthesis in the MSS-1 reactor, in a water-50% ethanol solution. Details of the experimental method are described in ref. [10]. The reaction was carried out in a mixture of water and ethanol as solvents, and the reactor MSS-1 was used [29]. The possibility to measure the reflected microwave power was exploited. A change in the reagents chemical composition would be reflected in a change of reflected power. It was found that reflected power increased after 16 min reaction time at 0.4 MPa and 220 °C. It was found that the change in this signal was correlated to the advancement of the reaction (Figure 12). The increase of the reflected power signal indicated that only 16 min reaction time was needed for the reaction to be completed. The use of the MSS process permits thus to control the reaction time within one minute time resolution, and stop it as soon as the reaction is accomplished. The specific surface area dropped from 320 m^2/g to 140 m^2/g after 16 min reaction time, which corresponds to crystallisation of NPs.

Figure 12. Relation between synthesis time and specific surface area during MSS synthesis of ZrO_2 nanoparticles in water, at 4 MPa reaction pressure.



The MSS technology was also applied for the synthesis of calcium stabilised nano-ZrO_2 particles in the size range of 7–10 nm, with narrow size distribution (dispersion 0.10) where the optimum structure was achieved by precise time control in the range of 33 min [30].

5. Conclusions

In the present paper, the preparation of nanoparticles of pure oxides, mixed oxides and phosphates via Microwave Solvothermal Synthesis, MSS, has been presented. This technology, also indicated as Microwave Hydrothermal Synthesis, MHS, when the solvent is water, is a process where liquid reagents are enclosed in a pressure vessel and are heated by means of microwaves. We have developed, designed and realized a reactor, MSS-2 type, which is able to produce nanomaterials in a chamber made from chemically inert alumina ceramic, at pressures up to 6 MPa and temperatures up to 260 °C, with reactions times controlled with 1 s precision. The reactor is suitable for large-scale production and industrial applications. We have also indicated the importance of sufficiently high MSS temperature or pressure for obtaining a fully reacted product. Thus, the main advantages of the MSS method: uniform heating with a rapid temperature rise, reduction of risk of contamination of the nanoparticles by reaction with heating elements and reaction walls, and precise control of reaction time, can be realised in an industrial scale production. In the example of hydroxyapatite synthesis, we could also show that precise control of reaction time possibly allows controlling the nanoparticles' properties.

Author Contributions

Witold Lojkowski is the main editor of the paper, wrote various segments of the text and the conclusions. Cristina Leonelli wrote the part on state of the art in microwave synthesis of nanoparticles and advantages of microwave solvothermal synthesis. Tadeusz Chudoba, Jacek Wojnarowicz and Andrzej Majcher cotrinbuted equally to the development and testing of the microwave reactors. Andrzej Majcher wrote the description of the MSS-2 reactor. Adam Mazurkiewicz supervised the construction of the above reactors.

Conflicts of Interest

The authors declare no conflict of interest.

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