Automation of the process of microwave hydrothermal synthesis of nanopowders

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Abstract: The article presents the process of microwave hydrothermal synthesis of nanopowders automation. The essential elements of automation are: a novel reactor and its control system. The reactor has a unique design of process chamber, which used in conjunction with a batch control system allows highly efficient production of nanopowders to be obtained. The design of the reactor together with new principles of operation, structural materials, and distribution of electromagnetic field are described. The paper also presents a control system for the reactor, which allows for automatic operation in the stop-flow mode, control of process pressure, continuous monitoring of process parameters and safe operation of the device.

Keywords: automation of chemical processes, microwave hydrothermal synthesis, stop-flow mode, batch control, nanopowders

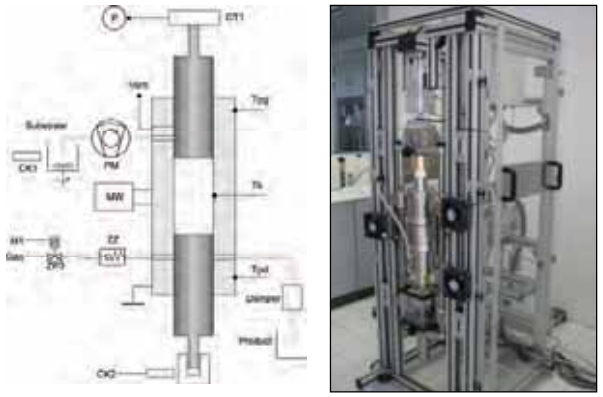
Microwave hydrothermal synthesis is one of hydrothermal processes that are used for the procurement of nanopowders with controlled chemical content and morphology characterised by minor differences in the size of the grains [1]. Application of microwaves significantly increases the speed at which synthesis takes place for ceramic materials (e.g. titanium oxide and oxides of other metals, hematite, barium titanate, lead zirconate titanate, lead titanate, potassium niobate) and metal powders including: nickel, cobalt, platinum, palladium, gold, silver and others [2]. Organic syntheses in which microwave radiation is applied form a separate group of synthesis reaction. This type of processes lead to the generation of, *inter alia*, various bioactive heterocyclic compounds, azides, thiocyanates and sulfones, or bimetallic systems including Pt–In, Ag–Pt, Pt–Fe, Cu–Pd, Pt–Pd, Pd–Fe, single and polyhedral nanotubes, composite materials [3, 4, 5, 6]. Majority of these materials are characterised by a high commercial potential, and can be applied particularly in electronic, optoelectonic, pharmaceutical, chemical, cosmetic, ceramic and machine industries.

Increase in the process kinetics by means of microwaves, which from the point of view of mass production is of great advantage, is unfortunately hampered by the lack of proper apparatus. Most of microwave hydrothermal synthesis reactions still take place in laboratory in modified microwave ovens. Commercial devices for microwave thermal syntheses with greater efficiency can be divided into: large closed vessel reactors, stop-flow reactors and flow reactors [7–10]. The advantages and limitations of all these types of reactors are present in numerous publications [11–16]. Main drawbacks of existing solutions from the point of view of mass production are as follows: low efficiency (in the case of large vessel reactors and stop-flow reactors), low flow of the substrate and the product of particularly thick suspensions in flow reactors.

1. A novel reactor with a moveable process batch

The reactor (fig. 1a, b) is a stop-flow type reactors. Substrates are fed through the dosing pump (PM) from the container equipped with a mechanical mixing system and a level sensor (CK1). Pressure (P) in the chamber is measured with the use of a strain gauge force sensor (CTa), and temperature with the use of thermocouples located on the outside of the top (T_{pg}) and bottom (T_{pd})

a) b)



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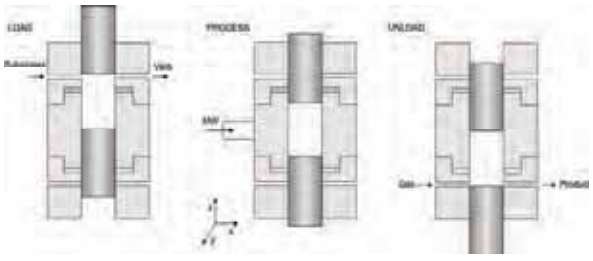


Fig. 1. General draft of the reactor (a), view of the prototype with the front cover taken off (b) principle of operation of the load and unload system (c)

Rys. 1. Schemat ogólny reaktora (a), widok prototypu ze zdjętą osłoną przednią (b) oraz zasada działania mechanizmu załadunku i rozładunku (c)

wall of the chamber and the thermocouple that is in contact with the Teflon batch in the chamber. The outflow of

the product can take place at the temperature and pressure of the reaction, which introduces an additional effect of quick drying. At low pressure of the product, the emptying of the chamber is supported by the neutral gas pressure or pressure of the air coming through the electromagnetic valve (ZP3) and the return valve (ZZ). The explosion protection system scatters kinetic energy of the bottom plunger and is controlled by the sensor (CK2).

A unique structure of the process chamber, uncommon for other solutions of this type, was applied in the reactor presented (fig. 1c). The structure is close 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 (MW) and chamber unload slots.

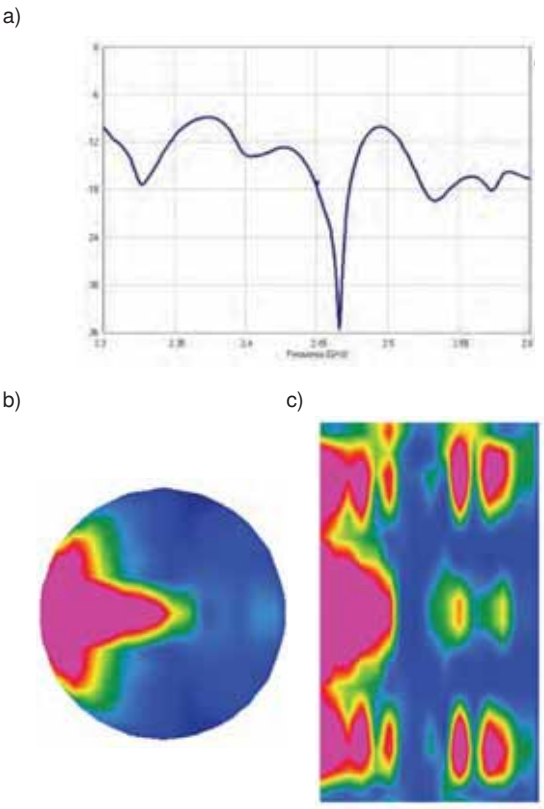


Fig. 2. Results of the analyses of the arrangement of the electromagnetic field for the MSS2 reactor: a) frequency characteristics for reflection coefficient $|S_{11}|$; b) distribution of average bulk density of power losses in the *xy* plane; c) distribution of average bulk density of power losses in the *xy* plane; scale 5 μW/mm^2, medium in the chamber – water

Rys. 2. Wyniki analiz rozkładu pola elektromagnetycznego reaktora MSS2: a) charakterystyka częstotliwościowa współczynnika odbicia |S11|; b) rozkład średniej gęstości objętościowej mocy strat w płaszczyźnie xy; c) rozkład średniej gęstości objętościowej mocy strat w płaszczyźnie xz; skala 5 μW/mm^2, medium w komorze – woda

All the elements that are in contact with the substrate and the product are made of chemically resistant materials – PTFE Teflon (connection lines, head of the dosing pump, middle part of the process chamber, seals) and Al_2O_3 ceramics (plungers, top and bottom part of the process chamber). Reaction pressure amounts to 6 MPa, which is obtained through the heating of the batch, however operation at higher pressure (up to 20 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 reactor is cooled down with the forced airflow.

The dimensions of the chamber were set with the use of computer simulations (QWED) so that the best adjustment of the chamber to the microwave generation path could be achieved, no leakage of microwaves at the ends of the plungers prevented, and a homogenous arrangement of the electromagnetic field ensured (fig. 2).

The microwave track of the device includes a generator with the 3 kW magnetron and a proper feeder (ERTEC Poland). The track is also equipped with two reeds located in the waveguide connecting the circulator with the process chamber, which together with reflected power measurement system allows for the system to be adjusted at the time of the process.

2. Process control

The main tasks realised in the process control system include:

- Regulation of process parameters;
- Superior control of processes;
- Monitoring and record of processes;
- Security and emergency states maintenance.

For the regulation of pressure (fig. 3), due to maximum speed of temperature rise and high delay caused by the microwave magnetron feeder, a two-phase regulator with hysteresis was applied.

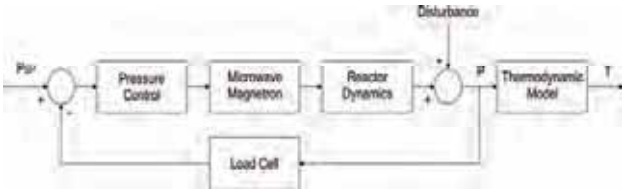


Fig. 3. Block diagram of pressure *P* regulation system and process temperature *T* determination

Rys. 3. Schemat blokowy układu regulacji ciśnienia *P* i wyznaczania temperatury procesu *T*

The dynamics of the object can be determined with the use of the balance of power supplied to the reaction chamber. Power of the microwave generator P_0 is partly reflected and the power that is actually supplied to the chamber is power P_e:

$$P_e = \eta P_0 \tag{1}$$

where: η – Power supply efficiency coefficient.
The power absorbed by the substrate is defined with the following:

$$P_e = 2\pi f \varepsilon_0 \varepsilon'' E^2 V \tag{2}$$

where:
f – microwave radiation frequency,
ε_0 – electric permittivity of vacuum, $\varepsilon_0 = 8.85\ 10^{-12}$ F/m,
ε'' – dielectric dissipation

E – electric field intensity with frequency f,
V – batch volume, $V_{max} = 400$ ml.
Power P_e is changed into heat Pt and by means of convection(P_c) and radiation (P_r) lost:

$$P_e = P_t + P_c + P_r \tag{3}$$

$$P_t = mc_w \frac{dT}{dt} \tag{4}$$

$$P_c = \alpha S(T - T_a) \tag{5}$$

$$P_t = mc_w \frac{dT}{dt} \tag{6}$$

where:
m – batch weight,
c_w – actual heat of batch
T – temperature in re action chamber,
t – time of temperature rise,
α - convection coefficient,
S – field of external surface of chamber,
T_a – temperature of the surrounding,
ε – emissivity,
σ –Stefan-Boltzmann's constant, $\sigma = 5.67\text{x}10^{-8}$ W/(m^{2}K^4).
Transforming equations (2)–(6) the following formula for the determination of the speed of temperature increase can be obtained:

$$\frac{dT}{dt} = \frac{2\pi f \varepsilon_0 \varepsilon'' E^2 V - \alpha S(T - T_a) - \varepsilon \sigma S T^4}{mc_w} \tag{7}$$

Solution to this equation for real synthesis process poses a lot of difficulties. The water dielectric dissipation coefficient is a non-linear temperature function. Additional problems occur in the case of mixtures that also contain non-polar ingredients [17]. Nonlinearity of the object is also visible in the case of work of the pressure regulator (fig. 4).

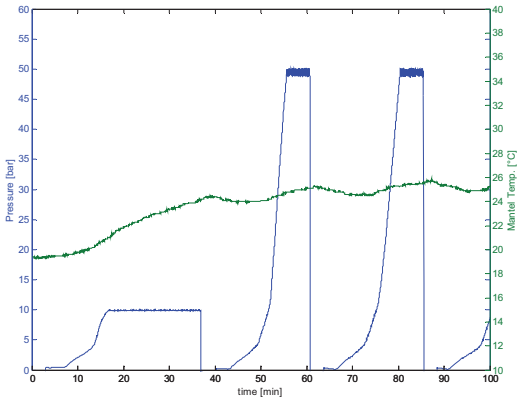


Fig. 4. Pressure and temperature course in the chamber: P_{sp1} = 10 bar, P_{sp2} = 50 bar, batch – deionised water 350 ml

Rys. 4. Przebieg ciśnienia i średniej temperatury płaszcza komory, P_{sp1} = 10 bar, P_{sp2} =50 bar, wsad – woda dejonizowana 350 ml

Temperature T is measured according to the following water thermodynamic model [18]:

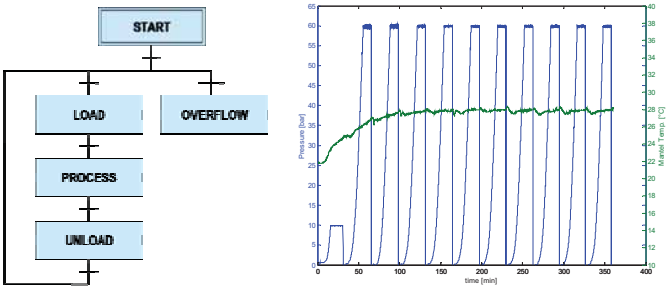
$$P = A10^{\left(\frac{mT}{T+T_n}\right)} \tag{8}$$

where: A, m, T_n – coefficients depending on temperature changes.

Maximum error occurs in the range of 200–350 °C and it amounts to 0.59 %. The measurement of the steam saturation temperature in the control system has an informational character and is not applied in the control process.

Superior process control is realised according to the PN-EN 61512 norm for the control of batch processes. In this control the realization of the process takes place automatically with the use of a procedure (technological recipe) which contains single phases of the process.

a) b)



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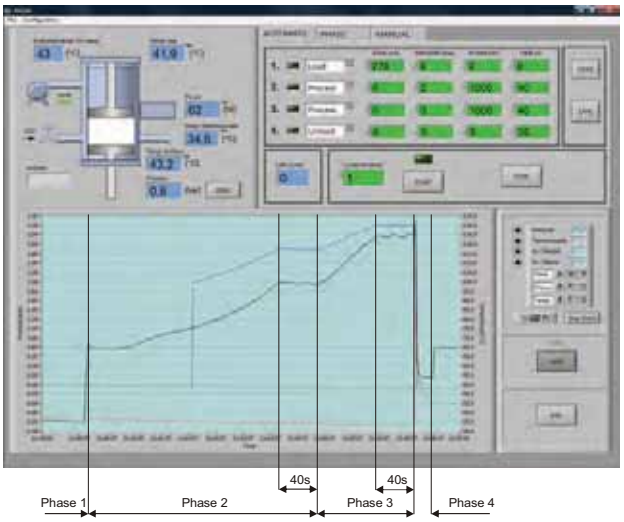

Fig. 5. Automatic (procedural) process control: a) process phases; b) course of process variables for cyclical recurrence of technological recipe realisation; c) image of the window of the control programme after realisation of a single recipe: Phase 1 – Load (278 ml), Phase 2 – Process (2 bar, 1 kW, 40s), Phase 3 – Process (3 bar, 1 kW, 40 s), Phase 4 – Unload (0, 20 s)

Rys. 5. Sterowanie proceduralne (automatyczne) przebiegiem procesu: a) fazy procesu; b) przebieg zmiennych procesowych dla cyklicznych powtórzeń realizacji receptury technologicznej; c) widok okna programu sterującego po realizacji pojedynczej receptury: Faza 1 – Load (278 ml), Faza 2 – Process (2 bar, 1 kW, 40 s), Faza 3 – Process (3 bar, 1 kW, 40 s), Faza 4 – Unload (0, 20 s)

The process is divided into phases of (fig. 5a): chamber load, process, chamber unload, chamber overflow, with the following parameters: *Load* (V), *Process* (p_p, P, t_p), *Unload* (p_u, t_u), *Overflow* (V, t_u), where:
V – batch volume,
p_p – pressure in the process chamber,
P – power of microwave generator,

t_p – pressure regulation time,
p_u – level of pressure at which process chamber is opened,
p_u – 0 stands for immediate opening of the chamber,
t_u – process chamber scavenge time.

Consecutive realisation of the stages is equivalent with the realisation of the process with the aforementioned parameters set (fig. 5c). The realisation of the process may also take place in the phase control mode in which each of the phases is realised as a single task, or in the manual control mode, in which each unit of the reactor can be switched on individually with the parameters set.

In automatic control the cyclical repetition of the programmed technological recipe is possible (fig. 5b), which leads to the automatic processing of the prepared volume of the substrate.

The system controls suitability of phase conditions (i.e. no pressure in the process chamber for the load phase, or presence of substrates in the process chamber for the process phase). Realisation of each of the phases can be paused manually at any time and the process can be resumed once a new sequence of procedural control is programmed, or the paused process stopped by the realisation of appropriate phases in phase control and the procedural control with the current technological recipe resumed.

Technological recipes are stored in text sets. The software allows for the use of formerly programmed recipes and their design in form of text sets in different environments than the main programme of the device.

Alarm and security procedures implemented in the control system constitute a supplement to hardware security. Emergencies are divided into levels connected with:
- condition of the device,
- setting of process parameters,
- initial conditions of process realisation phases,
- real values of process parameters.

Condition of the device is measured in the real time mode with the frequency of reading, in the control computer, of 1 Hz. This includes the following discrete stages: four side panels (removed, installed), state of the magnetron feeder (preparation to operation, readiness), pressure of air supplying pneumatic systems (too low, proper), activation of the explosion system, jamming of the plungers of the process chamber, level of fluid in the dosing pump container. The incorrect value of the state signal blocks the possibility for the realisation of processes.

Parameter setting is limited to nominal ranges. This concerns parameters of functions realised in manual, phase and procedural control modes.

Initial conditions for the realization of process phases are also checked in each of the control modes. All possible collisions are specified as follows:
- shift of plungers of the process chamber to the top position at the chamber pressure value above zero. This causes dosing pump damage or the rupture of the line through which substrates are fed,
- ignition of microwave heating when the process chamber is totally empty or filled in 10% only. This leads to the damage to the microwave track (circulator, magnetron) or overheating of chamber Teflon batch.

In the case of the above listed situations, the programme informs the user and prevents the realization of collision likely control procedures.

Real values of process parameters concern analogue signals, particularly pressure in the process chamber of the reactor, which is measured at the frequency of ca. 0.5 kHz and controlled by the PLC controller in the device.

Protection against microwave radiation constitutes an important safety aspect. Measured according to the PN-EN 55011 norm ("Industrial, medical and scientific devices with radio frequency") average values of electromagnetic disturbances do not exceed 70 dB (μV/m). The measurements were taken with the use of the FSH 8 electromagnetic field meter (by Rohde & Schwarz) with the HE 300 aerial (by Rohde & Schwarz) in the place where the reactor was installed. The device is also equipped with WPM-1 radiation indicator (ERTEC Poland) for constant monitoring of the level of microwave radiation emission.

The reactor was applied for the production of nanocrystal zinc oxide (ZnO-NPs) and nanocrystal zinc oxide mixed with cobalt (ZnO:Co-NPs) [19, 20].

3. Summary

The original architecture of the reactor presented allows full automation of the process and the procurement of nanopowders on a significantly greater scale than in the case of the application of laboratory equipment. It radically speeds up the realization of the process and enables to obtain products measured in litres, not as in the case of laboratory apparatus, millilitres.

The size of the process chamber does not influence excessive disturbances in the homogeneity of the distribution of the electromagnetic field and the existing heterogeneity of this distribution causes spontaneous mixing of the batch and prevents the creation of points with increased temperature.

A significant advantage of the reactor consists in the maintenance, owing to the application of chemically neutral materials, of high cleanliness of reaction and low sensitivity to substrates of high density, suspensions with sedimentation tendencies included.

The control system enables automatic realization of processes with consideration of operator and environment safety aspects and allows to easily include the device in a complex technological line.

Nanopowders obtained in the device are characterized by low distribution of grain size, high purity, and high production recurrence, which confirms the usefulness of the device in chemical, pharmaceutical and cosmetic industries.

4. References

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Automatyzacja procesu mikrofalowej hydrotermalnej syntezy nanoproszków

Streszczenie: W artykule przedstawiono automatyzację procesu mikrofalowej hydrotermalnej syntezy nanoproszków. Jej zasadniczymi elementami są: nowy typ reaktora oraz jego system sterowania. Reaktor posiada unikatową konstrukcję komory procesowej, co w połączeniu z zastosowanym systemem sterowania wsadowego pozwala na uzyskiwanie dużej wydajności produkcji nanoproszków. Opisano konstrukcję reaktora z uwzględnieniem nowej zasady działania, materiałów konstrukcyjnych, rozkładu pola elektromagnetycznego. Przedstawiono system sterowania urządzeniem, który zapewnia automatyczną realizacje procesów w trybie stop-flow, regulacje ciśnienia procesu, ciągłe monitorowanie parametrów procesów oraz zachowanie bezpieczeństwa obsługi urządzenia.

Słowa kluczowe: automatyzacja procesów chemicznych, mikrofalowa synteza hydrotermalna, stop-flow, sterowanie wsadowe, nanoproszki

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