Stand for Studies of Material Transformation During Fast Microwave Heating[1]

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Abstract – A stand for studies of microwave material heating is described and first experimental results are presented and discussed. Microwave heating has advantages compared to traditional heating methods, like uniform and volumetric sample heating, which provides high temperature increase rate for dielectric heating. The created experimental stand is a rectangular waveguide designed for 2.45 GHz frequency excited by a magnetron with power up to 2 kW. Novel technique for temperature measurement of matter in microwave field is suggested using. This tool uses high thermal conductivity of a thin BeO ceramic rod with thermocouples located on its surface outside the waveguide. Series of experiments were performed on microwave heating of various materials such as inorganic salts, metal powders, graphite, organic salts of nickel and cobalt, and ceramics.

1. Introduction

Microwave heating has several advantages over conventional heating methods which use heat conduction or radiation. In conventional heating, the energy is deposited at the surface of the material and the resulting temperature gradient causes the heat transfer into the core of an object. In microwave heating, the radiation penetrates the material and electromagnetic energy is directly converted into heat in the entire volume. Since the heating rate is not limited by heat conduction from the surface layer, the material can be heated more quickly. It also makes possible to reduce temperature gradients typical for furnaces, and achieve better uniformity of heat deposition. These features allow intensification of chemical reactions and thermal processing of materials [1–4]. Among practical applications of microwave heating are ceramics drying and sintering, thermal decomposition of complex chemical compounds like minerals and organic salts, acceleration of reactions, enhancement of catalyst efficiency, selective impact on magnetic materials.

2. Choice of Applicator Scheme

In order to benefit from the listed unique abilities of microwave heating, one needs to design microwave applicators with the desirable electromagnetic field distribution, to know dielectric, magnetic and thermal properties of studied materials, including temperature and frequency dependencies, to develop reliable and reproducible methods of temperature measurement.

Selection of an applicator scheme depends on dimensions and properties of samples and on conditions required for their processing. Since we started from studying samples with sizes 1–3 cm, much smaller than the wavelength of the utilized microwave radiation $\lambda_0 = 2\pi c/\omega = 12.2$ cm in free space, we chose a single-mode applicator, namely a rectangular waveguide working in TE_{10} mode. The electric field in this configuration has maximum in the middle of the wider wall where we place a sample.

Material heating by microwave radiation depends on two critical parameters, the dielectric constant ε', and the dielectric loss factor ε''. The dielectric constant describes the degree to which the material is polarized by an electric field, and the dielectric loss factor measures the efficiency of electromagnetic energy conversion into heat. Also the dielectric loss tangent is used $\mathrm{tg}\delta = \varepsilon''/\varepsilon'$, which characterizes the ability of the material to absorb and convert the electromagnetic energy into heat.

3. Temperature Measurement

Temperature of samples in microwave background is usually measured by thermocouples and pyrometers. In our case the use of pyrometer is hampered by elongated configuration of the quartz tube containing the sample and by material changes during microwave processing, such as vapor, powder blowout, color change, which all can lead to errors in temperature estimation. Thermocouples are widely used for temperature measurements in microwave applicators and

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give reliable results if their conductors are oriented exactly perpendicularly to the microwave electric field and have a grounded metal sheath in order to avoid arcing. These conditions limit the applicability of thermocouples to single-mode systems, in which the electric field pattern can be calculated precisely [1, 5, 6].

In our microwave stand the hole for sample insertion is made in the wide wall of the waveguide. The electric field in the TE_{10} mode is normal to this wall, which automatically excludes the possibility to use thermocouples inside a sample located in the waveguide, because there would be some parts of conductors aligned along the electric field. For our experimental conditions we suggested a new diagnostic tool, a thin cylindrical rod made of BeO (beryllium oxide) ceramics. One end of the rod is put in direct thermal contact with the heated sample, and high thermal conductivity of this ceramics allows us to use thermocouples outside the waveguide. The essence of the method is in favorable combination of unique features of BeO ceramics, which has very high thermal conductivity 270 W/m °C, melting point above 1700 °C, dielectric constant $\varepsilon' = 7$, and loss tangent $\mathrm{tg}\delta \approx 4 \cdot 10^{-4}$ (weak absorption of microwaves) [7].

Heat transfer along a thin ceramic rod can be described by one-dimensional equation $c\rho\partial T/\partial t = K\partial^2 T/\partial x^2$, where $T(x)$ is the sample temperature at point x, K is the thermal conductivity, c is the specific heat, and ρ is the density. Thus, the process of temperature distribution establishment along the rod is determined by the temperature conductivity coefficient $\kappa = K/c\rho$, which in case of BeO ceramics is about 1 cm^2/s. For comparison, $\kappa = 0.008$ cm^2/s for quartz glass, and 1.2 cm^2/s for copper. It means that in our experiments quartz is a good thermal insulator and BeO ceramics conducts heat almost as well as copper. From the heat conductivity equation one may estimate the typical time of temperature profile establishment along the rod $\tau \sim L^2/\kappa$, where L is the distance between the two selected points of the rod. For a thermocouple mounted on the probe at the $L \sim 5$ cm distance from the heated sample, we obtain that the sample temperature will be correctly estimated from the thermocouple data in $\tau \sim 30$ seconds. Thus, the use of this probe is justified if the sample temperature changes on a time scale large compared to the characteristic time of the probe τ. In the steady state the microwave heating is balanced by conventional heat transfer via thermal conductivity from the sample to colder parts of the stand through the probe and across the material supporting the sample (quartz tube or corundum powder), and by infrared emission.

4. Microwave Stand

The major part of the experimental stand for microwave heating is a rectangular waveguide with a cross section dimension of 90 by 45 mm which works in the TE_{10} mode and is excited by a domestic oven magnetron LG 2M214-39F with power supply tuned up to 2 kW at the frequency 2.45 GHz. The distances between the microwave exciter, test region where the sample is placed and waveguide ends are chosen so that the electric field is maximum in the test region, and the microwave power reflected back to the magnetron is minimum. In the test region a ∅15 mm quartz tube with the sample and ceramic probe with thermocouples is inserted through the hole in the wide wall of the waveguide (Fig. 1). The tube is connected to the vacuum pump for removal of gases, which may release from the sample during heating. In order to reduce the standing wave coefficient, the radiation passing through the test region of the applicator, is directed through a plastic window to the dummy load consisting of a waveguide filled with streaming water both for radiation absorption and cooling.

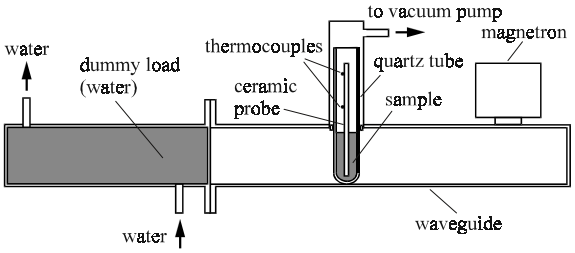

Fig. 1. Schematic of the microwave heating system

Geometry of the applicator was chosen on the basis of computer simulation of electromagnetic field inside the waveguide. The optimum scheme is presented in Fig. 2, where only one half of the waveguide is shown and another half is obtained by mirror reflection of the picture about $x = a/2$ plane. Because of partial wave reflection from the water load, the standing wave pattern is formed instead of the single pure TE_{10} traveling wave, as it should have been in case of the matched load at the waveguide end. As one can see in Fig. 2, a, the electric field is maximum in the test region where the sample is placed. If we assume the traveling wave amplitude E_0, then after adding of the absorbing water load, the maximum field increases to $E_{\max 1} \approx 1.7E_0$. Since wave propagation in the waveguide significantly depends on sample material and size, careful matching of the load with the applicator was not carried out. When a sample consisting of a water cylinder 0.8 cm in diameter and 4 cm long is placed in the test region, the wave pattern changes substantially, and the field amplitude in the test region increases to $E_{\max 2} \approx 4.5E_0$ (see Fig. 2, b). Water has very high dielectric constant $(\varepsilon' \approx 80)$, and therefore strongly affects the field distribution. In real experiments we test ceramic and powder samples with dielectric constant $\varepsilon' \sim 10$, thus the field pattern should not be distorted so much. Under microwave radiation

the water present in the sample is heated, evaporated and leaves the test region of the waveguide upward along the quartz tube making no affect on further heating and reactions in the sample. Thus, the drying of the sample takes place first, and consecutive heating is determined by dielectric properties of the sample itself in dry form.

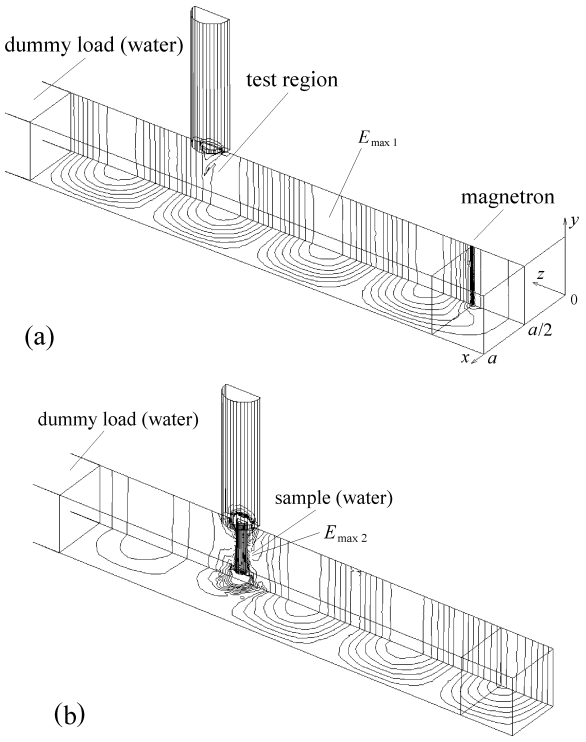

Fig. 2. Lines of constant absolute electric field in the microwave waveguide: a – without sample, b – with water sample

5. Experimental Results and Discussion

In our first experiments on microwave heating we used materials with known dielectric properties and their combinations: NaCl, aluminium powder, graphite in various modifications, powder corundum (α-phase of Al_2O_3) etc. The novel method of temperature measurement using the BeO probe was tested as well.

We started experiments on microwave irradiation of organic salts of nickel and cobalt $[LiAl_2(OH)_6]_2$M*edta*·nH_2O (DHAL-M*edta*), where the metal M stands for nickel or cobalt, *edta* is the ethylenediamine-tetraacetic acid, and DHAL is the layered lithium-alumimium double hydroxide. Nickel and cobalt can produce nanosized metal particles during thermal decomposition of such organic salts [8, 9]. In the cited works, the initial powder was heated using conventional methods to ~150–200 °C for water removal from the sample and then after heating above the threshold of 350 °C occurred thermal decomposition of Ni *edta* into metal nickel particles of typical size about 4 nm embedded in the parent organic layered matrix. Appearance of the metal nickel in reaction products is a good qualitative indicator of achievement of 350 °C temperature when the thermal decomposition occurs.

The experiments revealed several peculiarities of microwave heating of Ni *edta* powder. Fig. 3 demonstrates the temperature behavior measured by two thermocouples mounted on the ceramic rod inserted into the studied sample. The distance from the sample to the first thermocouple is $h_1 = 5$ cm, and to the second one $h_2 = 9$ cm. From the temperatures on both thermocouples one can make a simple estimate of the sample temperature by linear extrapolation: $T \approx T_1 + (T_1 - T_2)\,h_1/(h_2 - h_1)$.

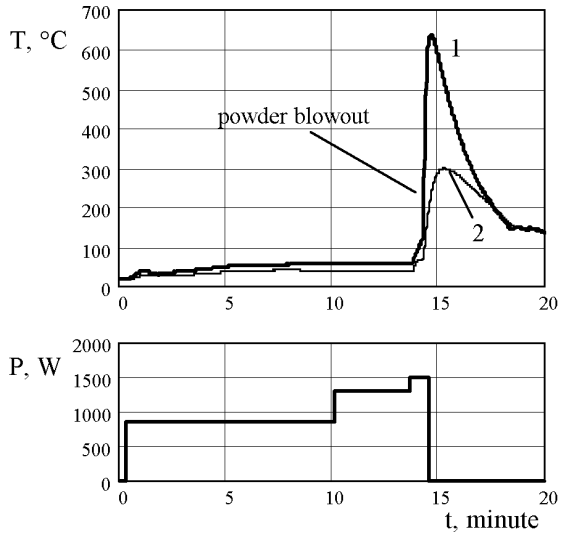

Fig. 3. Heating dynamics for $LiAl_2(OH)_6]_2Ni{\cdot}nH_2O$ powder. Temperatures at lower (1) and upper (2) thermocouples and magnetron power are shown

After microwave startup, the sample temperature increased to ~ 100 °C, and this level apparently did not depend on microwave power in the range from 300 to 1000 W, pointing probably at evaporation of moisture absorbed from air and of the hydrated water chemically bound in the substance. Evaporation is energy consuming, therefore there is a balance of heating and cooling which maintains the temperature ≤ 100 °C. When the powder was gradually dried, the steady state temperature was quite moderate, because microwave absorption by dry substance occurred to be low. However, when the power was increased to 1500 W, we saw the apparent powder heating much above the level required for the thermal decomposition. Visual control of the reaction products showed that there happened a blowout of powder from the test region into the upper part of the tube, and some black substance deposited on the tube wall and probe while the initial powder was light-blue.

Powder X-ray diffraction patterns of the reaction products revealed the presence of nickel nanoparticles, similar to those observed after conventional heating. It means that microwave heating led to partial thermal decomposition of the initial compound. These pre-

liminary qualitative results suggest that microwave processing can be efficient for fast heating and thermal decomposition of the described chemical compounds.

Another direction of our first experiments was the study of possibility to use microwaves to affect drying and sintering of ceramics. Much work in this field is carried out, showing that microwave processing can increase ceramic sintering rate, reduce processing temperatures, allow creation of more uniform samples and process magnetic materials [1–4, 6, 10].

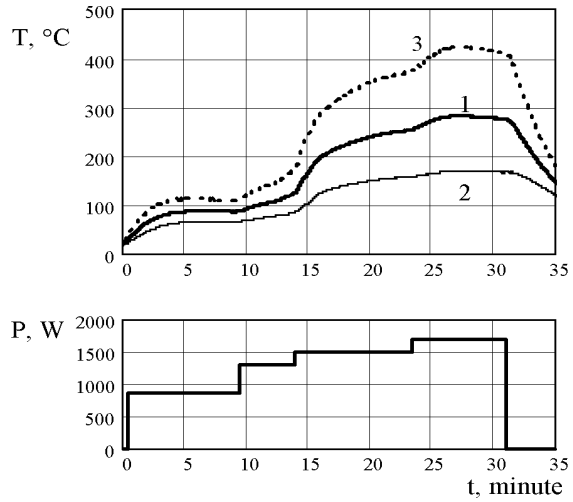

Fig. 4. Heating dynamics for $Gd_{0.4}Ce_{0.6}O_x$ + $LaMnO_3$ ceramics. Temperatures at lower (1) and upper (2) thermocouples, 3 – estimated sample temperature. Below is shown the magnetron power

We performed preliminary experiments on microwave heating of several ceramics. For better thermal insulation the samples were placed into corundum (α-phase of Al_2O_3) powder which has relatively low microwave absorption, high melting temperature ~ 2000 °C and is chemically passive. A sample of dried but not sintered ZrO_2 ceramics could not be heated above 200 °C even at 1300 W microwave power. In case of $Gd_{0.4}Ce_{0.6}O_x$ + $LaMnO_3$ ceramics (provided by Prof. V.A. Sadykov from the Institute of Catalysis, Novosibirsk, Russia) we managed to heat a cylindrical sample with diameter and length about 1 cm made of pressurized components for this ceramics up to 400–500 °C (Fig. 4). No doubt that this temperature is insufficient for ceramics sintering which happens at 1300 °C, but the obtained result allows us to suppose that using a high Q-factor resonator instead of a simple waveguide, and replacing the temperature probe conducting away substantial portion of the heating power, and using better thermal insulation of the sample, it will be possible to increase the sample temperature to values required for ceramic sintering.

6. Summary

The experimental stand for studies of material modification using microwave radiation at 2.45 GHz was created, and first experiments on heating of various materials with temperature control were carried out. As a next step in this work, the waveguide will be replaced by a high Q-factor single-mode resonator, which will increase the electric field amplitude in the test region.

Further studies are planned on elucidation of the optimum regimes of thermal decomposition of organic compounds with the goal to produce ultrafine metal powders. Experiments on microwave processing of ceramics for their property modification will be also continued. An adequate physical and numerical model of microwave heating accounting for realistic field distributions and heat balance is also required for better understanding and predictability of the heating process.

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