The research of ceramic materials for applications in the glass industry including microwave heating techniques

K.Kogut, K.Kasprzyk, B.Zboromirska-Wnukiewicz, T.Ruziewicz,
Electrotechnical Institute Division of Electrotechnology and Materials Science
Wrocław,
Skłodowskiej – Curie Street 55/61, 50-369 Wrocław, Poland

E-mail: k.kogut@iel.wroc.pl

Abstract. The melting of a glass is a very energy-intensive process. Selection of energy sources, the heating technique and the method of heating recovery are a fundamental issue from the furnace design point of view of and economic effectiveness of the process. In these processes the problem constitutes the lack of the appropriate ceramic materials that would meet the requirements. In this work the standard ceramic materials were examined and verified. The possibilities of application of microwave techniques were evaluated. In addition the requirements regarding the parameters of new ceramic materials applied for microwave technologies were determined.

1. Introduction
The microwave sintering initiated in mid 60th is currently an area of extensive research [1]. The microwave technique enable the fast and uniform heating of small and big shapes, removing volatile elements (binders, moisture, etc.) from big volumes and allow to reduce the thermal stresses in the heated material. 

Rising interest in the melting and sintering process via microwave is a results of time saving and a consequence of more homogeneous structure and improved properties of final products. The microwave heating of materials is completely different from the conventional heating method, which the energy transfer to inside of the material is a result of thermal conductivity [2].

Microwave processing of the materials, includes heating and sintering, is fundamentally different from the conventional processing involving radiant/resistance and/or convention heating followed by transfer of thermal energy via conduction to the inside of the work – piece through thermal conductivity mechanism.

Figure 1 illustrates some distinguishing features between the conventional and the microwave heating.

Great advantage of the microwave technologies application in relation to conventional methods, during glass melting, are significantly reduced emission levels of harmful substances to the atmosphere by elimination or at least mitigation of mine raw materials used. The decrease of the emission of greenhouse gases emission is a necessary action for slowing down the global climate change. In the case of furnaces supplied by fossil fuels, the realized thermal energy is connected with fuel combustion but also with emission of CO₂, SO₂, NOₓ and dusts.

In figure 2 types of influences of microwaves on different kinds of materials are presented.
Significant barrier for applying the microwave technology in the process of glass melting is the lack of the appropriate ceramic materials meet requirements:
- resistance against temperatures up to 1600 °C,
- stress resistance temperature (desirable low thermal expandability),
- wearability through the stream of the molten glass,
- corrosion resistance in gasses emitted by the molten glass,
2. Materials and methods
In this work the available ceramic materials were examined. Modified materials for application in microwave heating techniques were prepared. These materials were heat-treated. Based on the literature [5, 6], the adequate temperature of sintering was applied. A density and a porosity of the samples were determined by hydrostatic weighing method.
For research purposes the materials based on the alumina oxide, magnesia and the soapstone characterized by a low dissipation dielectric factor talking about the possibilities of heating materials in high frequencies, were used (tab. 1).

Table 1. Various materials used during experiments

| Material A, A<sub>L</sub> | Material B, B<sub>L</sub> | Material C, C<sub>L</sub> | Material D, D<sub>L</sub> | Material E - Steatite |
|-------------------------|-------------------------|-------------------------|-------------------------|-----------------------|
| Composition based on:   |                         |                         |                         |                       |
| MgO                     | Al<sub>2</sub>O<sub>3</sub> – Hungarian Clay “Jaroszow” | MgO                     | Al<sub>2</sub>O<sub>3</sub> – Hungarian Clay “Jaroszow” | Talc, Plastic Clay, Feldspar |
| Al<sub>2</sub>O<sub>3</sub> – Martinswerk Clay “Jaroszow” | Al<sub>2</sub>O<sub>3</sub> – Martinswerk Clay “Jaroszow” | Al<sub>2</sub>O<sub>3</sub> – Hungarian Clay “Jaroszow” |                        |                       |

A<sub>L</sub>, B<sub>L</sub>, C<sub>L</sub>, D<sub>L</sub> – preliminary cooled to – 23 °C,

Dissipation dielectric factor value was measured with aid of RF impedance/ Material analyzer Agilent E4991A.

A microwave device with the power of 1 kW was used to measure the speed of ceramic materials heating. Samples in the form of popular ceramic fittings were under constant microwave influence by the period of 30 minutes. The increase of the temperature by the pyrometer Abatronic AB infrared – 8859, with measurement range of temperatures from -50 °C to 1600 °C and the 50:1 optical resolution was carried out.

 Samples were also tested to evaluate mechanical strength. This particular property is important from the ceramic materials point of view e.g. as high-temperature crucible pots to microwave furnaces. The mechanical strength was appointed by three point bending tests with the use of the Rauenstein machine type 2143 with the measuring scope from 0 - 5 kN. Samples in the form of flattened circular cross – section bars with dimensions about 9.0 x 10.0 x 75 mm were used for examinations.

3. Results

3.1. Bulk density, porosity and absorbability

Bulk density, porosity and absorbability were determined with the use of the Polish Standard PN-89/E-06307 [7]. The results are showed in figure 4.

The highest density due to the lowest porosity and the absorbability was measured for sample B<sub>L</sub> sintered at temperature of 1430°C. In order to obtain high porosity [9, 10] to limit the heating of materials every type of samples was cooled to the temperature -23°C. The highest porosity was measured for the sample B<sub>L</sub> sintered at temperature of 1100°C.
3.2. The electric permittivity and tg delta measurements

Results of the electric permittivity and tg delta of measurements for particular materials are showed in figure 5 and in table 2.
Table 2. Results of the electric permittivity and tg delta of measurements in high frequencies for examined materials

| Material A | ε'< x10^1 | ε'' x10^-1 | tgδ x10^-3 |
|------------|------------|------------|-------------|
| sintered in 1100 °C | 3.83 | 3.68 | 3.44 | 3.59 |
|             | 3.29 | 2.03 | 1.03 | 1.44 |
|             | 86.1 | 55.2 | 29.8 | 40.2 |

| Material B | ε'< x10^1 | ε'' x10^-1 | tgδ x10^-3 |
|------------|------------|------------|-------------|
| sintered in 1100 °C | 5.12 | 4.72 | 4.26 | 4.38 |
|             | 3.67 | 1.12 | 4.38 | 1.44 |
|             | 71.6 | 49.3 | 9.74 | 33.0 |

| Material C | ε'< x10^1 | ε'' x10^-1 | tgδ x10^-3 |
|------------|------------|------------|-------------|
| sintered in 1100 °C | 4.37 | 4.18 | 4.09 | 4.11 |
|             | 2.83 | 1.88 | 1.00 | 1.57 |
|             | 64.7 | 45.0 | 24.4 | 38.1 |

| Material D | ε'< x10^1 | ε'' x10^-1 | tgδ x10^-3 |
|------------|------------|------------|-------------|
| sintered in 1100 °C | 5.00 | 4.75 | 4.23 | 4.46 |
|             | 3.80 | 2.33 | 2.73 | 1.17 |
|             | 75.9 | 49.0 | 6.46 | 26.3 |

| Material E | ε'< x10^1 | ε'' x10^-1 | tgδ x10^-3 |
|------------|------------|------------|-------------|
| sintered in 1280 °C | 5.33 | 5.01 | 4.42 | 4.42 |
|             | 4.91 | 3.70 | 2.29 | 4.74 |
|             | 92.0 | 74.0 | 51.8 | 107 |

For comparison, in table 3 the results of the electric permittivity and penetrability for popular ceramic materials applied in microwave heating techniques, were presented.
Table 3. Influence of microwaves on the popular ceramic materials [4].

| Type of the materials                  | ε'  | ε'' | Temperature [°C] | Penetration depth of microwaves [cm] |
|----------------------------------------|-----|-----|------------------|-------------------------------------|
| Alumina Oxide (Al₂O₃)                  | 9,00| 0,004| Room            | 1460                                |
| Alumina Oxide (Al₂O₃)                  | 9,46| 0,01 | 296             | 600                                 |
| Alumina Oxide (Al₂O₃)                  | 10,15| 0,055| 683             | 113                                 |
| Alumina Oxide (Al₂O₃)                  | 11,18| 0,241| 1221            | 27                                  |
| Silica glass (SiO₂)                    | 3,78| 0,00023| 25            | 16700                                |
| Sapphire (Al₂O₃)                       | 9,40| 0,00023| Room          | 26474                                |
| Silicon carbide (SiO₂)                 | 3,50| 0,00035| Room          | 10410                                |
| Silicon carbide (SiO₂)                 | 4,00| 0,04 | 2000            | 97                                  |
| Zirconium Oxide                        | 18,00| 2,34 | 300             | 4                                   |
| Zirconium Oxide                        | 22,30| 8,25 | 800             | 1                                   |

3.3. Investigation of the speed of heating for the commonly used ceramic materials

A microwave device with the power of 1 kW was used to investigate the speed of heating for the commonly used ceramic materials and materials prepared in this work (tab.1). Samples were put into constant microwave influence by the period of 30 minutes. Results of measurements are showed in figure 6 and 7.

![Figure 6. Speed of the common ceramic materials heating under the influence of microwaves.](image-url)
It was found that materials prepared in the work based on the $\text{Al}_2\text{O}_3$, MgO and steatite are characterized by lower temperature of heating in the same time and at the same power of the microwave device, than other popular ceramic materials. The samples at high frequencies have a low dielectric loss factor and high porosity. Therefore, the heat generated in material by the dielectric loss factor is lower than the other samples.

3.4. The mechanical bending strength

The mechanical bending strength was determined for the 5 samples, each of the measured materials. To calculate the mechanical bending strength the following equation according to PN IEC 60672 – 2 clause 6.5 [8], was used:

$$ R_g = \frac{8 \cdot F_s \cdot l}{\pi \cdot s \cdot d^2} \text{[MPa]} $$

where:

$ F_s $ – bending force,
$s$, $d$, $l$ – dimensions of the bars respectively: width, height, length

The results are shown in figure 8.

Figure 7. Speed of the ceramic materials A, B, C, D, E heating under the influence of microwaves.

Figure 8. The results of the mechanical bending strength for samples sintered in 1100°C and 1430°C.
It was noticed the increasing trend of higher mechanical bending strength for samples sintered at temperature 1430 °C then samples sintered in 1100 °C. The largest impact on the value of the mechanical strength was observed for the sample of material A. The addition of magnesium oxide and high quality alumina oxide with fragmentation 80% <10 μm, along with sintering at the temperature above 1400 °C improves the Rg value several times.

4. Conclusions
- The microwave techniques intended for sintering or melting of the glass can save the energy spent during the heating process. In addition the advantage is lower temperature or shorter time of sintering.
- Ceramic materials based on the alumina oxide, magnesia and the steatite during attempts with using the microwaves generator with the power of 1 kW are heated up to lower temperatures than other examined materials. The samples at high frequencies have a low dielectric loss factor and big porosity.
- Materials with lower rate of dissipation factor weren’t heated up so intensively like another’s. These losses are connected with dispersion of the energy via warming of the dielectric.
- Samples sintered in the same temperatures, preliminary cooled to the temperature - 23 °C were characterized by higher porosity than non cooled samples,
- Sintering of the samples based on magnesium oxide, high quality alumina oxide with fragmentation 80% <10 μm, at temperature above 1400 °C, improves the quality of this process and mechanical bending strength of this materials.

5. References
[1] Menezes R, Souto P, Kiminami R 2012 Sintering of ceramics – New Emerging Techniques. Microwave Fast sintering of ceramic materials chapter 1 3–26
[2] Oghbaei M, Mirzaee O 2010 J. Journal of Alloys and Compounds 494 175-189
[3] Agrawal D 2006 J. Transactions Of The Indian Ceramic Society 65 (3) 129-144
[4] http://wichary.eu
[5] Fu P, Lu W, Lei W, Xu Y, Wang X, Wu J 2013 Transparent polycrystalline MgAl2O4 ceramic fabricated by spark plasma sintering: Microwave dielectric and optical properties J. Ceramics International 39 2481-2487
[6] Zhou D, Xueman P, Kai C, Ziliang W 2012 Enhanced dielectric properties of alumina ceramic substrate for microwave application J. IEEE International Symposium on Radio-Frequency Integration Technology (RFIT) 101-103
[7] Polish Standard PN-89/E-06307 Electroinsulation ceramic materials
[8] Polish Standard PN IEC 60672 – 2 Insulation materials: ceramic materials and glass
[9] Gregorová E, Past W, 2011, Journal of the European Ceramic Society 31, 2073–2081
[10] Xue W, Sun Y, Huang Y, Xie Z, Sun J, Preparation and Properties of Porous Alumina with Highly Ordered and Unidirectional Oriented Pores by a Self-Organization Process, 2011 J. Am. Ceram. Soc., 94 [7] 1978–1981
Corrigendum: The research of ceramic materials for applications in the glass industry including microwave heating techniques

*IOP Conf. Ser.: Mater. Sci. Eng.* 113 (2016) 012014

K.Kogut, K.Kasprzyk, B.Zboromirska-Wnukiewicz, T.Ruziewicz, Electrotechnical Institute Division of Electrotechnology and Materials Science Wrocław, Skłodowskiej – Curie Street 55/61, 50-369 Wrocław, Poland

Description of corrigendum:

**Page 2:**

Figure 3 replaced

Figure 3. The example of microwave glass furnace 120 kg – produced by Plazmatronika NT sp. z o.o. Wrocław