Differential Thermal Analysis in Microwave Hybrid Field of Some Composite Ceramic Materials

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Abstract. Microwave heating is a green technology that provides many advantages over conventional heating. In this paper, we analyse some composite ceramic materials, formed by barium carbonate and hematite powders. There were used three mixtures with micron, submicron and nanometric particles size. All the mixtures were sintered in microwave hybrid field using a new differential thermal analysis technique. For this type of materials it was necessary to optimize the heating process and has been found that the microwave sintering time is very short, in the order of minutes, compared to resistive heating, which is a great advantage in terms of process productivity. Using differential thermal analysis in microwave hybrid field, the sintering temperatures of the magnetic ceramic materials could be identified. The sintering temperature of the sample from nanometric powder mixture decreased by about 20% compared to the sintering temperature of the sample from micron powder mixture. The use of the nanometric mixtures in experiments is advantageous as it ensures high productivity, low sintering temperatures and very good magnetic parameters.

Keywords: Differential thermal analysis · Microwave sintering · Ceramic materials

1 Introduction

Microwave energy has been increasingly and successfully used in the past and it will be highly used in the future to process materials with unique properties at high temperatures (>1000 °C) in a broad range of traditional and emerging manufacturing fields of materials such as ceramics, metals or in nanotechnology [1–7].

Today industry is pursuing higher performance and competitive costs. In order to achieve these objectives, new technologies and production methods are becoming a necessity. Many technologies are facing challenges in their transition to sustainability. As an important contribution to a sustainable future, the industry and its products must be adapted to a circular economy —a system aimed at eliminating waste, circulating, and recycling products, and saving resources and the environment [8, 9].

Microwave processing has appeared as a flexible form of energetics with many improvements over conventional heating, the most important of which are: shorter time

I. Dumitru et al. (Eds.): ICOME 2022, AHE 15, pp. 441–448, 2023.
https://doi.org/10.2991/978-94-6463-152-4_49

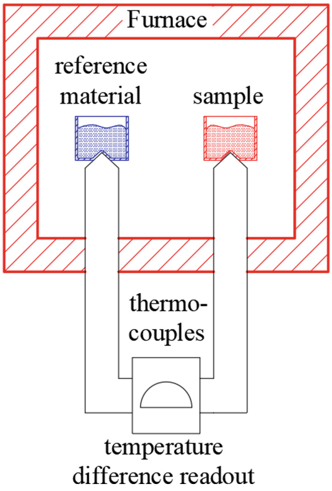


Fig. 1. DTA technique

cycles, significant energy savings, and higher quality of the final material [10–13]. All these advantages, both energetic and economic, create a new vision for the future of ceramic materials and their industrial manufacturing.

The widely used thermal analysis methods are differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermo-gravimetric (TG) analysis [14].

Differential thermal analysis is a technique which is similar to differential scanning calorimetry (DSC), in which the temperature difference between the sample and the reference material is monitored as a function of time or temperature. The reference and sample materials are kept at the same temperatures in the furnace to ensure that the testing environment is uniform. Classical DTA technique is presented in Fig. 1.

In this study, a new differential thermal analysis in microwave hybrid field (DTA-MHF) was developed to analyse the sintering range of some composite ceramic materials.

The limited thermal response using conventional heating is avoided using microwave heating as there is a direct interaction of the material with the microwave energy [15].

The ceramic composites used in the experiments were barium carbonate and hematite powders mixtures. The particles size of these mixtures started from micron area to nanometer area. The sintering method in microwave hybrid field has proven to be advantageous for powders containing nanometric particles.

2 Experimental Procedures

Three barium carbonate and hematite powder mixtures ($>99\%$ purity) were used. Powders were provided from ROFEP, Romania. The three mixtures are varied in terms of particle size, namely: the first mixture, coded M1, has micron sizes (~2 µm), the second mixture, coded M2, has submicron sizes (~0.7 µm) and the third has particle sizes of powders in the nanometer area (~90 nm).

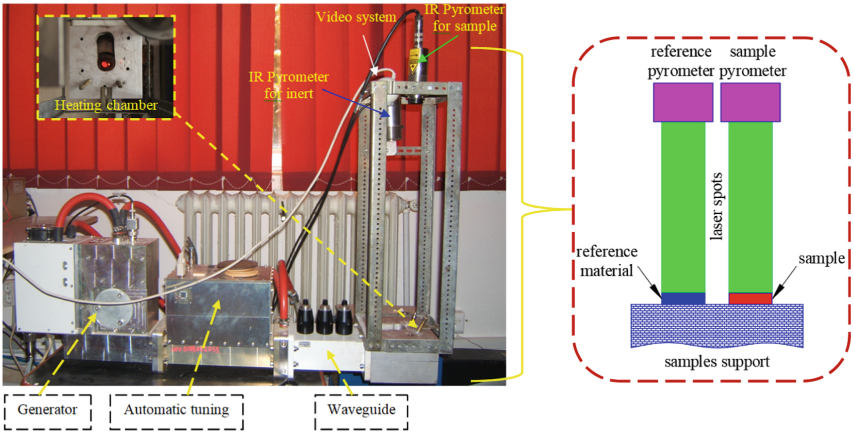


Fig. 2. Microwave heating device

The mixtures were compacted into pellets of 11 mm diameter and ~ 2 mm thickness at a pressure of ~ 320 MPa and then subjected to the microwave hybrid sintering, where DTA was determinate.

The sintered samples were measured by a Vibrating Sample Magnetometer in order to see if the samples have been sintered and have magnetic properties.

Description of the Differential Thermal Analysis Procedure in Microwave Hybrid Field Microwave heating is performed with high frequency electromagnetic waves which exclude the use of thermocouples or thermo resistors as temperature sensors.

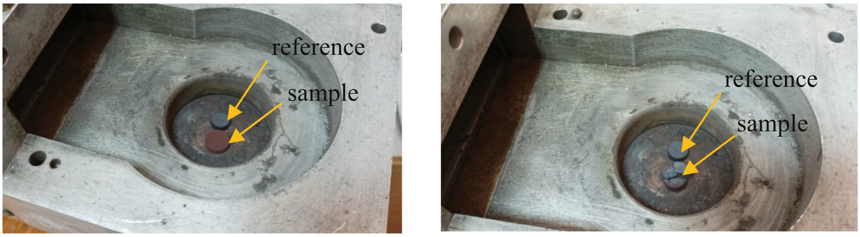
The microwave heating device is a Muegge Electronic GmbH (Germany) heating system with mono-mode heating chamber. The device consists of a microwave generator with a water-cooled magnetron having a maximum power up to 1250 W and is adjustable in the range 10–100%. The microwave installation has automatic tuner (Germany) which helps the microwave generator to transfer the maximum power to the samples from the heating chamber. The two infrared pyrometers (Germany), one for the sample and another for the reference, were used to measure the temperatures in the heating chamber.

An important condition to realise the experiments for DTA-MHF is to place the pyrometers at a short distance from each other in order to ensure to the two samples the same intensity of the electric field and therefore a similar heating.

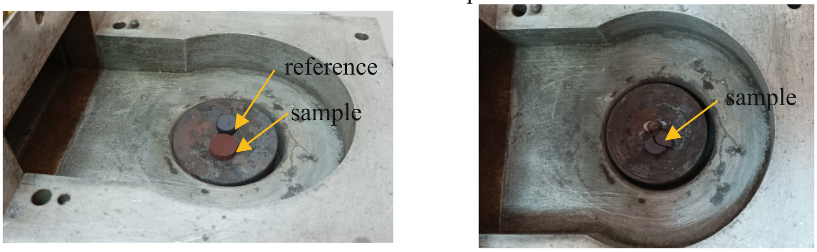
Heating chamber and position of the samples before and after DTA-MHF are presented in Fig. 3.

As it can be seen in Fig. 2 and 3, there are two products placed in the heating chamber. The sample has a diameter of 11 mm and the reference sample has a diameter of 10 mm, both made from the same materials.

To obtain the reference sample, it was used the classical DTA analysis, using a DTA device.



First attempt



Second attempt

Third attempt

a) b)

Fig. 3. Samples location in the heating chamber: a) before DTA-MHF; b) after DTA-MHF

3 Results and Discussions

The reference sample was formed in a DTA device with a heating up to 1500 °C and a constant speed of 10 °C/min. It was choose this temperature to eliminate all the phase transformations which can occur in the reference material and to assure this way that this material can be used as an etalon. Classical DTA of this material is presented in Fig. 4.

Can be seen in the diagram all the three curves (DTA, DTG and TG) and it is very clear presented that from 1100 °C to 1500 °C there aren't any decomposition or weight losses. So, the classical heated material can be used as a reference.

Both, reference material and the sample were placed in the heating chamber as it can be seen in Fig. 3. There were realised three attempts to optimise the microwave process.

In the first attempt we placed the products on the chamber's sheet plate. With the gradual increase of the injected power, was observed that a microwave plasma arc was generated in the heating chamber, which didn't allow increasing the temperature required

Fig. 4. Classical DTA diagram for the reference material

to sinter the sample. Due to repeated plasma arc, the sample broke and no sintering peak could be identified from the diagram.

In the second attempt we inserted a metal cylinder with a hole in the center in the microwave heater central place in order to position the samples at the level of the waveguide. In this way, the heating process was improved, but the phenomenon of electric arc occurrence was still not eliminated, and the temperature didn't reach the sintering level of the sample.

In the third and the last attempt we inserted a refractory cylindrical brick in the center of the microwave heater central place. In order to avoid the occurrence of electrical discharges between the samples and the heating chamber, it is necessary to use an electrical insulator between them. The refractory brick behaved like an electrical insulator to avoid electrical discharges between the samples and the heating chamber. The products were heated in microwave field up to 700 °C and after that the refractory brick transmitted the heat by conduction to the samples up to a temperature of 1100 °C. This type of heating is called hybrid field microwave sintering, and due to the fact that the DTA curve can be determined in this way it can be said that all the sintering process is called differential thermal analysis in microwave hybrid field (DTA-MHF). The refractory brick is replaced after one or two sintering processes because the smallest defect of it can lead to the early appearance of the electric arc, which can destroy the sample. All the three mixtures were sintered this way.

DTA-MHF diagram for the first mixture, with micronic particles, is presented in Fig. 5. There are presented three curves, first for sample, second for reference sample and the third for DTA. This diagram shows a peak on the DTA curve with corresponding on the sample temperature curve at a temperature of 1080 °C. The sintering time, up to 1080 °C, was 10 min.

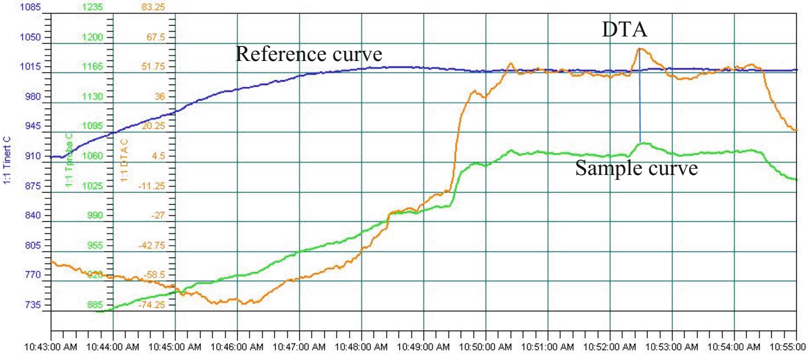


Fig. 5. DTA-MHF diagram for M1

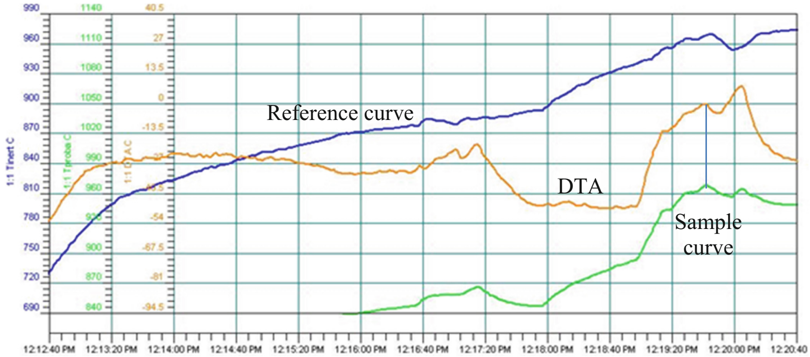


Fig. 6. DTA-MHF diagram for M2

DTA-MHF diagram for the second mixture, with submicron particles, is shown in Fig. 6. There is a peak at 970 °C on the DTA curve and the sintering time was about 8 min. DTA-MHF diagram for the third mixture, with nanometric particles, is shown in Fig. 7. The peak for the sintering temperature is located at 870 °C.

After plotting the DTA diagrams in microwave, the three samples were sintered again to the previously analysed peak temperatures, shown on the diagrams, and then cooled in water to avoid any adverse effects that could influence the magnetic parameters.

To verify that the samples were sintered, their magnetic properties were determined. The magnetic hysteresis loops of all the three samples are presented in Fig. 8.

For all 3 hexaferrite samples the values of the remanent magnetization far exceed the technical norm of 4 emu / g imposed in industrial production. The coercive field also has high values between 1200 and up to 2130 Oe. The nanometric dimensions of the powder particles have a great influence on the decrease of the temperature and time sintering but also on the properties of the magnetic materials during microwave heating. It can be concluded from Fig. 8 that the samples are sintered at those temperatures from DTA diagrams, due to magnetic properties obtained.

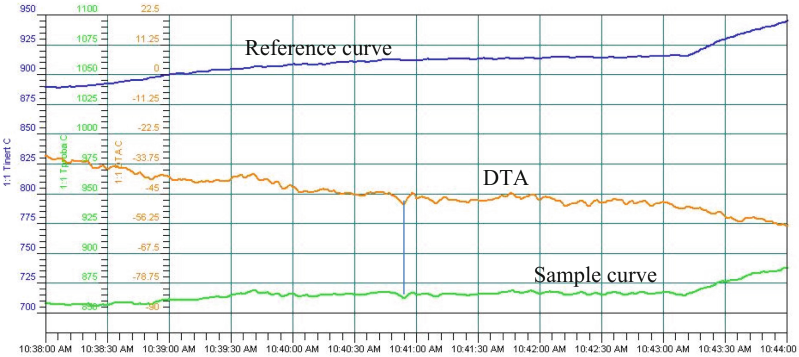
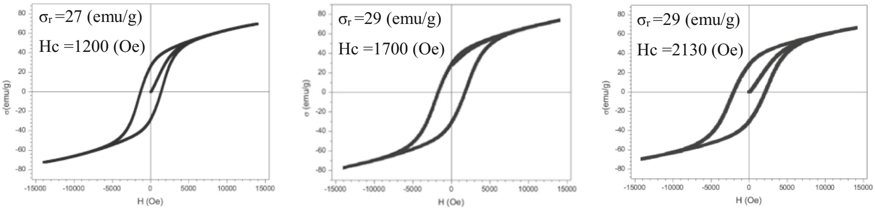


Fig. 7. DTA-MHF diagram for M3



a) M1 d) M2 e) M3

Fig. 8. Magnetic hysteresis loops

4 Conclusions

A new differential thermal analysis in microwave hybrid field of some composite ceramic materials was developed in this experimental research. It started from three barium carbonate and hematite mixtures with micron, submicron and nanometric particles size. Classical DTA technique was used in order to create the reference material and it was found that after 1100 °C the material no longer allows any change in its structure. Microwave heating process has been adjusted after three attempts. The pure microwave field was helped by the refractory brick to transmit the heat by conduction to the samples up to the sintering temperature. Sintering temperatures of M2 and M3 samples decrease compared to that of the M1 sample with significant values which represent 10% respectively 19%. Effective sintering of the samples takes place in a wide thermal and time interval in which the electric and magnetic field components of the electromagnetic radiation interact with the newly formed phase, which leads to an increase in the magnetic performance of the sample. The evolution of the coercive field values shows that the greatest influence has the fineness of the powders (M3 mixture with values of 2130 Oe) compared to the sample from submicron powders (M2 mixture with values of 1700 Oe).

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