Modified Ceramics Based on the Pyrolysis Residue of Municipal Solid Waste

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Abstract. To successfully solve the relevant problem of recycling solid household waste (SHW) in Russia, it is necessary to move from its landfill disposal to industrial processing. A promising option is the pyrolysis of solid carbon-containing waste, which can significantly reduce the amount of waste, as well as obtain alternative types of energy. The use of products of solid household waste pyrolysis as a method of production of ceramics is proposed. A new ceramic material was obtained where the solid residue of pyrolysis of an SHW mixture with average morphological composition was used as a structure-phase-forming additive. Chemical composition of the material, its average density, thermal conductivity and diffusivity, and specific heat capacity have been determined experimentally. It is recommended to use this ceramic material to manufacture building products for various purposes.

1. Introduction

More than a dozen technologies for processing solid household waste using various methods have been implemented worldwide. The most common are thermal method, like combustion, pyrolysis, and gasification.

Pyrolysis one of the more promising methods of processing solid household waste. It is both environmentally safe and makes its possible to obtain secondary useful products. Pyrolysis produces a combination of solid, liquid, and gaseous products in varying proportions by changing operating parameters such as temperature and rate. Thermal decomposition of waste can be carried out in such a way to produce gas and solid carbon residue with a minimum concentration or even complete absence of liquids, or obtain a liquid as one of the target products.

Of all the products formed during the pyrolysis, gaseous products have found the most widespread use. From the economics point of view, the use of pyrolysis gases as a fuel is considered beneficial. However, the possibility of such use is determined by the composition of gases, which depends on the technology of SHW processing. [1, 2]

Liquid fraction is usually used during pyrolysis to generate heat. Occidental Petroleum Corp has developed the method for obtaining liquid fuel (pyrofuel) using instant pyrolysis. [2]

Solid products (solid carbon residue) of household waste pyrolysis contain organic and inorganic components. One of the promising areas is its application in metalworking as a part of protective materials used in steel casting. [3] A number of researchers have developed technologies that make it possible to obtain molded fuel from the solid carbon-containing residue left during tire pyrolysis. [4, 5] Another area where pyrolysis residue is used is the production of various materials for industrial, civilian, and road construction, for example, cement or foam glass. [2, 6] However, the widespread
industrial application of solid carbon residue is currently insufficient, while the creation of energy-efficient non-waste technologies based on its use has great prospects.

We have proposed to use the solid carbon residue formed during the pyrolysis of SHW with an average morphological composition [7] as a structure-phase-forming additive to produce ceramics. Local clay may serve as a raw material for the production of modified ceramics.

The study of microstructural features of the pyrolysis residue samples was carried out using a TESCAN Vega 3SBH scanning electron microscope at an accelerating voltage of 60 kV. The microstructure of samples of carbon residue obtained during the pyrolysis of individual SHW components is shown in Fig. 1.

![Figure 1. Photos of samples of carbon residues obtained during pyrolysis: A) food waste, B) paper, C) wood, D) textile.](image)

The results of SEM analysis show that the pyrolysis residue retains the structure of the original material, but becomes brittle and black-gray in color.

Energy dispersive analysis (EDA) was carried out using an energy dispersive spectrometer based on a X-Max nitrogen-free detector (Oxford instruments), mounted on a TESCAN Vega 3SBH scanning electron microscope.

Elemental composition of carbon residue obtained during the pyrolysis of an SHW mix with an average morphological composition is shown in Table 1.

| Element | Weight % | Sigma weight % |
|---------|----------|----------------|
| C       | 66.34    | 0.23           |
| O       | 18.77    | 0.23           |
| Na      | 0.02     | 0.02           |
| Mg      | 0.29     | 0.02           |
| Al      | 0.04     | 0.02           |
| Si      | 0.11     | 0.02           |
| S       | 0.19     | 0.02           |
| Cl      | 0.40     | 0.02           |
| K       | 3.60     | 0.06           |
| Ca      | 9.61     | 0.15           |
| Ti      | 0.03     | 0.01           |
| Zn      | 0.04     | 0.02           |
| P       | 0.52     | 0.02           |
| Fe      | 0.02     | 0.01           |
| Total   | 100.00   |                |
The modified ceramic material was obtained as follows. First, the pyrolysis of a SHW mixture with an average morphological composition was carried out at 700 ℃. The resulting carbon residue was crushed to obtain a fine powder. At the second stage, low-melting and low-plasticity clay was mixed with a fine powder in a 4:1 ratio, and 12% of water was added until a homogeneous mixture was obtained. Samples were formed using a hand press. The obtained samples were dried in a drying oven and then fired in an electric furnace. At stage three, the resulting particulates were used as a leaner to obtain a ceramic molding powder with the following composition: clay and leaner in a 3:2 ratio, and the molding moisture content of 12%. Samples were formed from the resulting charge using a hydraulic press. Heat treatment was carried out in a drying oven and then in an electric furnace.

To determine the quantitative and qualitative composition of the obtained ceramic material, X-ray phase analysis was carried out using a DRON-3M diffractometer. Based on the data obtained, the authors have determined the chemical composition of the ceramic material, its main component being silica:

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\text{SiO}_2 - 53,7\%, \quad \text{Al}_2\text{O}_3\text{Si}_3\text{O}_{11} - 21,1\%, \quad \text{Fe}_2\text{O}_3 - 10,7\%, \quad \text{CaMgSi}_2\text{O}_6 - 14,5\%.
\]

Obtaining new materials, the properties of which are determined by such factors as physical and chemical transformations, heating rate, wide temperature range etc. requires experimental studies to determine their thermophysical features.

2. Study methods

The purpose of this study is to determine the thermophysical properties (TPP) (specific heat capacity, density, as well as thermal conductivity and diffusivity) of a ceramic material obtained using the pyrolysis residue of SHW. Experimental and calculation methods were used during this study.

To determine the thermal conductivity of the ceramic material, the well-known stationary method of a cylindrical layer [8] was employed. The experimental setup is shown in Figure 2.

According to this method, the material under study was shaped into a cylindrical hollow tube made up of nine short rings (1) tightly adjacent to each other. The length of the sample’s working section was 200 mm. The inner diameter \(d_1\) of the studied sample is 15 mm, the outer diameter \(d_2\) is 45 mm. To reduce heat losses, heat-insulating sleeves (2) were installed at the ends of the heater. An electric cartridge heater (3) was placed inside the material. The heater creates a heat flux uniformly distributed over the length of the sample. In the steady state of the system, the entire amount of heat that is released in the electric heater passes through the cylindrical layer of material.

The electric heater is powered via autotransformer (4) with stabilized voltage. The heater power was changed by changing the voltage in the heater circuit. The amount of heat released by the electric heater was determined according to the Joule-Lenz law. To do that, the voltage and current rate were measured using a voltmeter (5) and an amperemeter (6).
The temperatures of the studied material were measured using six Cr-Al DTPK 011-0.7 (t1 ... t6) thermocouples, the hot junctions of which were laid on the outer (t2, t4, t6) and inner (t1, t3, t5) surfaces of the studied material.

The temperature values were recorded using an MBA-8 analog input module. Data was transferred to a PC using an AC-4 converter (RS-485-USB). Temperature values were recorded using specialized software with a time interval of 1 sec. The temperature stabilized 90 min after the device had been turned on. The temperatures at the inner and outer surfaces of the cylinder were averaged over the readings of the corresponding thermocouples. During the experiment, the voltage was varied between 20 and 200 V. In this case, the power of the heater varied from 2.4 to 310.6 W, and the average temperature of the sample was between 30 and 515°C. Sample temperatures at a heater power of 36.4 W are shown in Fig. 3.

![Figure 3. Sample temperatures at 36.4 W: 1 – inner surface, 2 – outer surface.](image)

Using the obtained temperature values, the thermal conductivity coefficient was calculated according to this formula:

$$\lambda = \frac{Q \cdot \ln(d_2/d_1)}{2 \cdot \pi \cdot l \cdot (T_1 - T_2)}$$

where $d_1$, $d_2$ are inner and outer diameters of the studied cylinder respectively; $T_1$, $T_2$ are the temperatures at inner and outer surfaces of the cylinder.

A number of methods are known for the experimental determination of thermal capacity of solids. [9] In our research, we have used the calorimetric method. The installation used to determine the heat capacity of the material consisted of a calorimeter, a heater, a balance for weighing prototypes, and a thermocouple for measuring the water temperature in the calorimeter.

We have used the well-known formula to determine the thermal diffusivity of the material under study:

$$a = \frac{\lambda}{(c \cdot \rho)}$$

where $\lambda$, $c$ are heat conductivity and diffusivity coefficients obtained experimentally; $\rho$ is average density.

3. General results
Using the above methods, we have calculated the thermophysical coefficients of the new ceramic material.
The average density of the material was 1,752.6 kg / m³.

The obtained dependence of the thermal conductivity coefficient from the temperature range of 30 to 515 °C is shown in Fig. 4.

![Figure 4](image)

**Figure 4.** The dependence of the thermal conductivity coefficient of the modified ceramic material from the temperature range: 1 – experiment, 2 – approximation.

It is clear from looking at the figure that the thermal conductivity coefficient increases unevenly with increasing temperature. The obtained experimental data have been approximated by the equation \( \lambda = 0.243 + 2.83 \times 10^{-3} \cdot t - 7.012 \times 10^{-6} \cdot t^2 + 5.968 \times 10^{-9} \cdot t^3 \) with the reliability \( R^2 \) of 0.98.

The dependence of the average heat capacity from the temperature is shown in Fig. 5. The obtained data are approximated by a linear equation: \( c = 550.81 + 10.125 \cdot t \) with the reliability \( R^2 = 0.956 \).

Analysis of the results presented in Fig. 5 indicates the increasing nature of the specific heat of the material under study with increasing temperature.

![Figure 5](image)

**Figure 5.** The dependence of the modified ceramic material’s specific heat capacity from the temperature: 1 – experiment, 2 – approximation.

The dependence of the thermal diffusivity coefficient of the material under study and temperature was obtained using formula (2) and experimental data (Fig. 4, Fig. 5). Results are shown in Figure 6.
Figure 6. The dependence of the thermal diffusivity coefficient from the temperature: 1 – experiment, 2 – approximation.

The dependence of the thermal diffusivity from temperature, \( a = f(t) \), shown in Fig. 6 has decreasing nature.

The obtained data are approximated by a linear equation: \( a = 2.3094 \cdot 10^{-7} - 6.7246 \cdot 10^{-10} \cdot t \) with the reliability \( R^2 \) of 0.95.

The obtained data on the TPPs of the material under study are comparable with the TPPs of known ceramic materials [10, 11].

4. Conclusion
Authors have calculated and performed experimental studies of the thermophysical properties of a new ceramic material obtained using solid carbon residue of pyrolysis of a SHW mixture with an average morphological composition as a structure-phase-forming additive.

Temperature dependences of the average specific heat capacity and thermal diffusivity of the ceramic material in the range of \( 30 \text{C} \ldots 90 \text{C} \), and the thermal conductivity in the range of \( 30 \text{C} \ldots 500 \text{C} \) have been obtained. It is comparable with the thermophysical features of ceramic materials. Thus, it is advisable to use the pyrolysis residue of solid household waste instead of expensive additives to produce new ceramic products.

5. References
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