It’s known [1 – 8], that the enthalpy (H), thermal conductivity (\(\lambda\)), the coefficient of thermal capacity at constant pressure \(p = \text{const} (c_p)\) or specific volume \(\upsilon = \text{const} (cV)\), linear thermal expansion coefficient (\(\alpha\)), depends on the temperature (T), but there are missing: a thorough analysis of this relationship for metals, not given approximation for metals, not given approximation methods of корреляційного та регресійного аналізу і обґрунтоване визначення коефіцієнтів теплоемності, теплопровідності, лінійного коефіцієнта теплоового розширення та зміни енталпії від температури, порядкового номера та радіуса атома металів. Вивчене експериментальні дослідження теплофізичних властивостей композиційних полімерних матеріалів на основі політетрафторетилену, ароматичного поліаміду, полііміду та наповнювачів.

Поставлеються задачі вивчення залежності теплоемності, теплопровідності, лінійного коефіцієнта теплоового розширення та зміни енталпії від температури, порядкового номера та радіуса атома металів. Вивчені експериментальні дослідження теплофізичних властивостей композиційних полімерних матеріалів на основі політетрафторетилену, ароматичного поліаміду, полііміду та наповнювачів.

1. Introduction

The metals of I B group of the Periodic system elements were an object of research: copper, silver and gold, as well as composite materials based on aromatic polyamide (fenilon C-2), polyimide (PM-69) and polytetrafluoroethylene (PTFE 4) filled with high-strength graphite, carbon fiber from tape VMN-4, basalt fiber and colloidal graphite C-1. The properties of these materials are given in [9 – 14], where the classification of carbon fibers is defined in [15, 16]: HM – highly modular; PAN – with polyacrylonitrile fabric, ribbons or fibers; \(\rho = 1800 \text{ kg/m}^3\) – specific density of the fiber; \(\gamma = 1.0 \%\) – specific elongation at break, \(d_i = 6.0 \text{ microns}\) – the average diameter of the fibers; \(\sigma_i = 2.0–2.5 \text{ GPa}\) – tensile strength of the fiber; \(E_i = 240–300 \text{ GPa}\) – modulus fiber tensile; \(T_k = 2673 \pm 20 \text{ K}\) – final temperature thermal treatment of fibrous materials.

Basalt fibers obtained from deposits of minerals Berestoveckij and had the following characteristics: \(\rho = 2700 \text{ kg/m}^3; \gamma = 1–4\%; d_i = 11 \text{ microns}; \sigma_i = 1.8–2.2 \text{ GPa}; E_i = 93–114 \text{ GPa}\).

Colloidal graphite C-1 was obtained by thermal anthracite graphitization at 2773 ± 100 K, followed by grinding in a colloid mills. Graphite C-1 had the following characteristics: ash content of 1.5 %, moisture content 0.5 %, fineness of grinding: the particle size of 1–80 microns particle size of the main fraction 1–8 microns (75 %) the residue on the sieve with holes 63 microns – less than 0.5 %.

2. Work objective
The compositions based on polytetrafluoroethylene, aromatic polyamide and polyimide fibers and dispersions, powders of graphite or carbon fibers were obtained by CMA-technology [17]. Shredding source of carbon fibrous materials was carried out in the hammer mill KDU “Ukrainian” at 3000 rev./min. working groups, and then type knife grinders MRP-1 at 7000 rev./min. (frequency of rotation 117 s¹, the maximum speed of 78 m/s) 10 min. for carbon fibers and 20 min. for basalt fiber to obtain fibers with bulk density \( p = 30–50 \text{ kg/m}^3 \). Aromatic polyamide powders and fillers were mixed in Mills MRP-1 at 7000 rev./Min. 5 min. This mixing process was accompanied, however, with an additional decomposition of the polymer powders, graphite and fibers. Fibers before and after mixing were volume (mass) gamma-distribution and Weibull distribution for lengths in the range of 20 – 1200 microns [18]. Preparations were made by the technology of processing of aromatic polyamides compression [19]. The fibers were arranged randomly in layers that are perpendicular to the force pressing in the direction of deformation and heat flow in the study of thermal conductivity on temperature.

3. Experimental part

3.1. The tabular data was used for analysis [1]. Correlation and regression analysis were performed in [20 – 22]. Selective correlation coefficient of the relationship between y and x \( r_p \) was calculated by the formula [20, 21]. Zero hypothesis of equality to zero of general correlation coefficient was advanced.

\[
\rho = 0
\]

\[
H_0: \uparrow , \quad r_p \neq 0
\]

and also alternative hypothesis

\[
\rho \neq 0
\]

\[
H_1: \uparrow , \quad r_p \neq 0
\]

where the selective correlation coefficient was a statistically estimate of the general correlation coefficient:

\[
r_p \rightarrow \rho .
\]

The test \( H_0 \) was performed for a significance level \( \alpha = 0.05 \) and \( \alpha = 0.01 \) and degrees of freedom \( f \):

1. For a critical value of the correction coefficient \( r_{mp} \) [22];

2. In terms of Student’s \( t_f \) [21];

3. According to the Fisher transformation [21] and the product \( (z_f \cdot \sigma_z) \).

3.2. The thermal conductivity of the investigating polymer materials was measured by the apparatus ITЛ-400 in the monotonous mode of heating on cylindrical samples. Flat surfaces of samples were being grinded by fray powder on the control plate to surface roughness \( R_2 = 0.63 \). The measurements were performed according to standard techniques. While commissioning the measure ITЛ-400, calibration was provided. The measurements were performed in the temperature range 323 – 473 K over 25 K.

4. Results and discussion

The dependence of enthalpy change from temperature, serial number and radius of atom of metals has been analyzed and proved by correlation and regression analysis. Fig. 1 represents the dependence enthalpy (\( \Delta H \)) of copper, silver and gold from the temperature (T). It is shown that enthalpy is growing from \( \Delta H = 39.5 \text{ kJ/kg} \) to \( \Delta H = 463 \text{ kJ/kg} \) (for copper), from \( \Delta H = 23.8 \text{ kJ/kg} \) to \( \Delta H = 245 \text{ kJ/kg} \) (for silver) and from \( \Delta H = 13.3 \text{ kJ/kg} \) to \( \Delta H = 147 \text{ kJ/kg} \) (for gold) with the growth of temperature from \( T = 400 \text{ K} \) to \( T = 1357 \text{ K} \). With the growth of the serial number of metal enthalpy decreases (Fig. 1).

The dependence of coefficient of thermal conductivity from temperature, serial number and radius of atom of metals has been analyzed and proved by correlation and regression analysis [23]. It is shown that with increasing temperature for most metals thermal conductivity decreases. In Fig. 2 shows the dependence of thermal conductivity (\( \lambda \)) of copper, silver and gold from the temperature (T) in the temperature range 0–50 K (Fig. 2, a) and in the range 100–1300 K (Fig. 2, b). As can be seen from Fig. 2, a for gold (curve 3) observed a slight increase in the coefficient of thermal conductivity of \( \lambda = 200 \text{ W/m·K} \) with increasing temperature from \( T = 0 \text{ K} \) to \( T_{\text{max}} = 20 \text{ K} \). With further increase in temperature from \( T_{\text{max}} = 20 \text{ K} \) to 25 K coefficient of thermal conductivity slightly decreases from \( \lambda = 800 \text{ W/m·K} \) to \( \lambda = 439 \text{ W/m·K} \). For silver and copper (Fig. 2, a curve 1 and 2, respectively) observed a significant increase in the coefficient of thermal conductivity from \( \lambda = 4800 \text{ W/m·K} \) (for silver) and from \( \lambda = 500 \text{ W/m·K} \) (for copper) with increasing temperature from \( T = 0 \text{ K} \) to the temperature of the peak maximum of its value (\( T_{\text{max}} = 8 \text{ K} \) for silver and \( T_{\text{max}} = 15 \text{ K} \) for copper). With further increase in temperature from \( T_{\text{max}} = 50 \text{ K} \) coefficient of thermal conductivity decreases sharply from \( \lambda = 10600 \text{ W/m·K} \) (for silver) and from \( \lambda = 5000 \text{ W/m·K} \) (for copper). As shown in Fig. 2, b, the coefficient of thermal conductivity of metals: copper (curve 1), silver (curve 2), gold (curve 3) with increasing temperature from \( T = 100 \text{ K} \) to \( T = 1300 \text{ K} \) decreases linearly from \( \lambda = 500 \text{ W/m·K} \) (for copper), from \( \lambda = 431 \text{ W/m·K} \) (for silver) and from \( \lambda = 343 \text{ W/m·K} \) (for gold) and is independent of the atomic number of elements the metal.

Established that growth between coefficient of thermal conductivity and the radius of metal atoms no linear connection between a metals of periodic elements at temperatures 100, 200, 273, 300 and 900 K is close linear relationship [24, 25].

The dependence of coefficient of thermal capacity from temperature, serial number and radius of atom of metals has been analyzed. It is shown that with increasing temperature for most metals thermal capacity increases. Established that growth between coefficient of thermal capacity and the radius of metal atoms no linear connection between a metals of periodic elements at temperatures 100, 200, 273, 298 and 700 K is close linear relationship [26, 27].

In Fig. 3 shows the dependence of coefficient of thermal capacity (\( c_p \)) metal-subgroup of group Periodic system – copper, silver and gold – from the temperature (T) in the temperature range 0–200 K (Fig. 1, a) and in the range
200–1200 K (Fig. 1, b). As shown in Fig. 1, a, for gold (curve 3), an increase in the coefficient of thermal capacity from $c_p = 6 \times 10^{-6}$ to $c_p = 0.123$ kJ/kg·K, for silver (curve 2) a significant increase from $c_p = 7.2 \times 10^{-6}$ to $c_p = 0.225$ kJ/kg·K, for copper (99.99 %) (curve 1) increases sharply from $c_p = 14 \times 10^{-6}$ to $c_p = 0.356$ kJ/kg·K with increasing temperature from ~0 K to $T = 200$ K. The coefficient of thermal capacity with increasing atomic number of elements decreases. As shown in Fig. 1, b, the coefficient of thermal capacity of metals: copper (curve 1), silver (curve 2), gold (curve 3) with increasing temperature from $T = 200$ to $T = 1200$ K increases linearly from $c_p = 0.356$ to $c_p = 0.502$ kJ/kg·K (for copper), from $c_p = 0.225$ to $c_p = 0.267$ kJ/kg·K (for silver) and from $c_p = 0.123$ to $c_p = 0.142$ kJ/kg·K (for gold), depending on the serial number of elements the metal.

**Fig. 1.** Dependence of enthalpy change ($\Delta H$) from temperature (T) for: 1 – copper (Z = 29), 2 – silver (Z = 47), 3 – gold (Z = 79)

**Fig. 2.** Dependence of the thermal conductivity ($\lambda$) from temperature (T) for: 1 – copper (Z = 29), 2 – silver (Z = 47), 3 – gold (Z = 79): a - in the temperature range 0-50 K; b - in the temperature range 100-1200 K

**Fig. 3.** Dependence of the thermal capacity ($c_p$) from temperature (T) for: 1 – copper (Z = 29), 2 – silver (Z = 47), 3 – gold (Z = 79): a - in the temperature range 0-200 K; b - in the temperature range 200-1300 K

**Fig. 4.** Dependence of the linear coefficient of thermal expansion ($\alpha$) of the metal from the temperature (T): 1 – copper (Z = 29), 2 – silver (Z = 47), 3 – gold (Z = 79)

The dependence of linear coefficient of thermal expansion from temperature, serial number and radius of atom of metals has been analyzed and proved by correlation and regression analysis. It is shown that with increasing temperature for most metals linear coefficient of thermal expansion increases.
Fig. 4 represents the dependence of the linear coefficient of thermal expansion (α) of the metals subgroup of the periodic system elements – copper, silver and gold – from the temperature (T) in the temperature range 0-200 K (Fig. 4, a) in the temperature range 200-1250 K (Fig. 4, b) and in the range from 0 to 1250 K (Fig. 4, c). As shown in Fig. 4, a, linear coefficient of thermal expansion of metals with increasing temperature from ~ 0 K to T = 100 K rapidly increases from α = 0,008·10^{-6} to α = 10,45·10^{-6} (for copper), from α = 0, 02·10^{-6} to α = 14,7·10^{-6} (for silver), from α = 0,026·10^{-6} to α = 11,5·10^{-6} (for gold). Further increase in temperature from 100 K to 200 K leads to a slight increase of the linear coefficient of thermal expansion. As the Fig. 2, b in all three cases, linear coefficient of thermal expansion increases linearly, from α = 11,5·10^{-6} to α = 19,5·10^{-6} for gold (curve 3), α = 10,45·10^{-6} to α = 24,4·10^{-6} for copper (curve 1) and from α = 14,7·10^{-6} to α = 28,1·10^{-6} for silver (curve 2) with increasing temperature from T = 100 K to T = 1250 K. As shown Fig. 2, c with increasing temperature from ~ 0 K to 100 K linear coefficient of thermal expansion for Cu, Ag and Au intensively growing. In the range of high temperatures there is a slight increase in the linear coefficient of thermal expansion with increasing temperature in all three cases. Dependence α = f (T) is described by logarithmic equation with linear expansion coefficient does not depend from the serial number of elements.

Established that growth between linear coefficient of thermal expansion and the radius of metal atoms is linear connection between a metals of periodic elements at temperatures 100, 200 and 300 K, at temperature 800 K – no linear connection. Established that growth between linear coefficient of thermal expansion and the serial number of the metal atoms is linear connection at temperatures 100, 200 and 800 K, at temperature 300 K – no linear connection [28].

Explain the properties can be found as follows. During the solidification of metals (such as in the cooling melt) while the huge number of small crystals, which interfere with each other to grow and acquire the correct form. Therefore, any metal product has polycrystalline structure consisting of a large number of small crystals - the so-called crystallites, or grains, which, unlike the well-polished single crystals of other inorganic substances have irregular shape and different spatial orientation. For this reason, in the crystal structure of metals occurring defects that significantly affect the physical properties of metals.

Experimental investigation of thermophysical properties of composite polymeric materials based on polytetrafluoroethylene, aromatic polyamide and polyimide and fillers are explored. Thermophysical behavior of polyimide composites filled with graphite and carbon fibers have been studied in a wide temperature range. Fig. 5 represents the influence of the concentration of fiber (carbon fiber fabric with THN-2m) filler on the thermal properties of antifriction materials based on polyimide PM-69. Found that when injected in the composition of the carbon fiber fabric THN-2m in amounts up to 40 wt. % of the observed linear increase in thermal conductivity of the material temperature. In Fig. 5 clearly shows that the thermal conductivity increases linearly with increasing concentration of graphite fibers. This dependence increases with temperature tests. Two characteristic ranges have been revealed on concentration dependence: φ < 20 % vol. and φ > 40 % vol. Composite behavior has been found differ essentially beyond the limits indicated [29].

A significant increase in thermal conductivity of composites observed with the introduction of metal powders (Fig. 6). This is due to the fact that the filler content 20 vol. % or more, the role of surface phenomena at the interface of phases, as most of the substance enters the state boundary surface layers. Interaction of metal particles with macromolecules of the polymer prevents globule formation and shifts the mobility of interstitial segments in the boundary layer. This process involves the formation of aggregates of macromolecules of the polymer, which in turn is a consequence of the formation of donor-acceptor bonds between the metal particles and macromolecules of the polymer at the interface phases. This facilitated energy exchange processes and thus increases the thermal conductivity of the composite. Note that for materials with low conduction matrix and high conductive filler metal powder at concentrations 25-28 vol. % thermal conductivity of the composite decreases with increasing temperature. This phenomenon is due to the dominant role of the metal particles in highly filled polymer systems, for which the behavior of the composite in thermal repeats dependence of thermal conductivity of metal temperature.
In the absence of fillers (Fig. 7, curve 17), with minimal carbon fibers (3.4 mass fraction) (curve 8); with minimal graphite content (2.31 mass fraction) (curve 5), with a maximum content of carbon fiber, graphite and basalt fibers (Fig. 7, curve 7, Fig. 8, curve 10).

The thermal conductivity of composites based on PTFE-4 for temperature 298 K (Table 1).

<table>
<thead>
<tr>
<th>Filler</th>
<th>Volume-filler content, %</th>
<th>Calculated thermal conductivity (W/m·K) by the formulas</th>
<th>Experimental thermal conductivity (W/m·K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Maxwell-Aiken</td>
<td>Odelevskyi</td>
</tr>
<tr>
<td>Graphite C-1</td>
<td>20.0</td>
<td>0.42</td>
<td>0.41</td>
</tr>
<tr>
<td>Titanium</td>
<td>23.0</td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td>Carbon fibers (GC; LM; E_r = 37 GPa; \sigma_0 = 0.54 GPa; T_K = 1120 K)</td>
<td>26.7</td>
<td>0.49</td>
<td>0.49</td>
</tr>
<tr>
<td>Coke + Carbon fibers (GC; LM; E_r = 37 GPa; \sigma_0 = 0.54 GPa; T_K = 1120 K)</td>
<td>15.0+7.0</td>
<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td>Coke + Carbon fibers (GC; LM; E_r = 36 GPa; \sigma_0 = 0.49 GPa; T_K = 2670 K)</td>
<td>15.0+7.0</td>
<td>0.37</td>
<td>0.38</td>
</tr>
<tr>
<td>Coke + Carbon fibers (PAN; HM; E_r = 270 GPa; \sigma_0 = 2.2 GPa; T_K = 2670 K)</td>
<td>15.0+7.0</td>
<td>0.63</td>
<td>0.29</td>
</tr>
<tr>
<td>Powder copper + molybdenum disulphide</td>
<td>28.0+2.6</td>
<td>0.52</td>
<td>0.52</td>
</tr>
<tr>
<td>Powder nickel + molybdenum disulphide</td>
<td>28.0+2.6</td>
<td>0.52</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Fig. 7. Dependence of thermal conductivity (\lambda) from temperature (T) for compositions based on aromatic polyamide.

The largest thermal conductivity are compositions containing the maximum amount of graphite, the lowest thermal conductivity are compositions containing a minimal amount of graphite. The effect of temperature is most noticeable in the compositions of the maximum and minimum content of carbon fiber, graphite and basalt fibers (Fig. 7, curve 7, Fig. 8, curve 10).
The effect of high concentrations (graphite C-1) filler on the thermal properties of antifriction materials based on polyimide PM-69 (Fig. 9). Found that when injected into the composition structure of graphite C-1, the thermal conductivity initially increases linearly with increasing filler content (up to 30 % by mass), and then when the content of graphite C-1 more than 30 % by mass, this figure increases dramatically, which can be explain the formation of conductive channels at a given concentration of graphite. Accordingly, it has returned linear approximation equation (Fig. 9):

\[ \lambda = 0.0009T + 0.0615 \text{ for curve 1 (a = 0 %);} \quad (4) \]
\[ \lambda = 0.0008T + 0.286 \text{ for curve 2 (a = 10 %);} \quad (5) \]
\[ \lambda = 0.0016T + 0.3173 \text{ for curve 3 (a = 20 %);} \quad (6) \]
\[ \lambda = 0.0012T + 0.6867 \text{ for curve 4 (a = 30 %);} \quad (7) \]
\[ \lambda = 0.0043T + 0.582 \text{ for curve 5 (a = 40 %).} \quad (8) \]

The total error ranged from 1.5 – 6.99 % when the temperature \( T = 298 – 473 \text{ K} \) and the concentration of graphite C-1 \( C = 0 – 40 \text{ %}. \)

6. Conclusions

1. The temperature dependence of thermal conductivity and thermal capacity, enthalpy changes and linear coefficient of thermal expansion of the metals: copper, silver and gold were studied, their approximation dependences were received.

2. After the results of correlation analysis, we set the relation between the coefficient of thermal conductivity, coefficient of thermal capacity, enthalpy change, the linear coefficient of thermal expansion and the radius of atoms and atomic number of metals under certain temperatures. Value of linearity and nonlinearity was given; the dependence between the coefficient of thermal conductivity, coefficient of thermal capacity, enthalpy change, the linear coefficient of thermal expansion and the radius of atoms and atomic number of metals under certain temperatures was generalized.

3. New correlations of dependence of thermal conductivity from temperature and concentration for composite materials were received on the basis of polytetrafluoroethylene, aromatic polyamide and polyimide and fillers.

4. The fact was set, that the coefficient of thermal conductivity of the studied polymers increases with increasing temperature.

5. The influence of the nature of particulate and fibrous fillers on the thermal properties of antifriction materials was researched. Ushering graphite powder with different dispersion and ash or carbon fibers with different structures and the degree of carbonization and graphitization in compositions, based on aromatic polyimide, one can develop antifriction materials with desired coefficient of thermal conductivity.

References


5. Лукьянов, А. Б. Физическая и коллоидная химия [Текст] / А. Б. Лукьянов
7. Фролов, Ю. Г. Физическая химия [Текст] / Ю. Г. Фролов, В. В. Белик
72. Базюк, Л. В. Теплофізичні властивості металів та стопів: 2. Залежність коефіцієнта теплопровідності від температури та електропровідності // Базальто-волокнистые композиционные материалы и конструкции.
62. Базюк, Л. В. Теплофізичні властивості металів та стопів: 3. Залежність коефіцієнта теплоємності від температури та електропровідності // Базальто-волокнистые композиционные материалы и конструкции.
52. Базюк, Л. В. Теплофізичні властивості металів та стопів: 4. Залежність лінійного коефіцієнта теплового розширення від температури та електропровідності // Базальто-волокнистые композиционные материалы и конструкции.