Structure and thermophysical properties of polytetrafluoroethylene-aluminum composite materials produced by explosive pressing

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Abstract. Metal filled composite materials on the basis of polytetrafluoroethylene (PTFE) are widely used in tribotechnical units of different equipment. Amongst the metal fillers for PTFE, aluminum is the most perspective, it has high thermal conductivity and low density, which is relevant for the aircraft industry. Due to low adhesion of PTFE to metals, the thermal conductivity and strength properties of these CM are low, so it is perspective to use explosive pressing (EP) which provides the conditions for an increase in physical-chemical interaction between CM components. The work researches the influence of EP on the structure, thermal expansion and thermal conductivity of composite materials on the basis of PTFE containing 10 and 30% vol. of aluminum. It has been established that EP, as well as sintering in a closed volume, contributes to a decrease in thermal expansion and an increase in the thermal conductivity of composite materials, which is connected to structural changes accompanied by an intensification of adhesive interfacial interaction. At the same time, with an increase in aluminum concentration, the efficiency of EP increases due to the increase in the number of contacts between metal particles, as well as the occurrence of an interphase zone, with peculiar properties.

1. Introduction
Polytetrafluoroethylene (PTFE) is often used [1] for production of tribotechnical units, it has a uniquely low coefficient of friction, chemical and thermal resistance, vibration absorption [2]. However, due to low wear resistance, thermal conductivity and high cold flow, pure PTFE is not used in practice, but compositions with metallic fillers are [3, 4]. In order to manufacture aviation tribotechnical units, PTFE is filled with light aluminum, high thermal conductivity of which contributes to the removal of heat from the friction zone. The use of explosive pressing [5,6] and sintering in the closed state is relevant in the creation of a strong adhesive interaction between PTFE and filler. During the friction process, a large amount of heat is released, which can strongly affect the PCM, leading to a large thermal expansion and local overheating. Therefore, such properties as thermal expansion and thermal conductivity are important characteristics of the antifriction materials’ performance [7].

2. Methods
Comparative studies of the effect of static (SP) and explosive pressing (EP) on the thermophysical properties of composite materials based on PTFE, filled with 10 and 30% vol. powdered aluminum PA-4 with a dispersion of 100-200 μm, the particles of which have a spherical shape. Volume proportions were provided by mixing the weights of a given mass (accurate to 0.01 g) suspended in the laboratory
weighing scales OHAUS-123. Static pressing of the samples is carried out in one-sided molds under pressure of 200 MPa. Explosive pressing is carried out by an ampoule scheme under a pressure of 0.4-0.8 GPa. Sintering is carried out in a free and closed state at a temperature of 380°C with a holding time of 15 minutes per one millimeter of the sample’s cross section. Sintering in the closed state is carried out in a special mold.

CM microstructures were investigated with "Olympus" BX-61 optical microscope in reflected light. The density was measured by hydrostatic weighing with the Shinko HTR-220CE analytical scales according to GOST 15139-69. The quantitative phase relation was calculated by the additivity rule using the data about density and monitored by examining the structures using the AnalySYS program. The thermal expansion of the filled PTFE was measured using a Hyperion Netzsch 402 F3 uniaxial thermomechanical analysis system. The samples had a height of 2 mm and a diameter of 5 mm, heating is carried out up to 390°C at a rate of 3°C/min, and the measurement is conducted along the direction of the pressing. The thermal expansion curves were constructed and analyzed using the Proteus 61 firmware. The values of cited thermal expansion are the result of approximation of experimental data obtained by testing at least 3 identical CM samples. The coefficient of thermal conductivity (λ) was measured at room temperature (22°C) in accordance with the standard KIT-02TS "Teplofon" installation procedure. The quantitative phase relation was calculated according to the additivity rule in correspondence with the density data and monitored by examining the structures using the AnalySYS program.

3. Results
It has been established that with the increase of aluminum content from 10 to 30% the density is increasing from 2215-2300 to 2310-2395 kg/m³ (figure 1), which is close to the theoretical density, calculated by the additivity rule (density ρ_{Al} = 2700 kg/m³ and ρ_{PTFE} = 2150-2280 kg/m³). After sintering the statically pressed samples, both in the free (figure 1, columns 2) and in the closed state (figure 1, columns 3), the density decreases. Moreover, sintering in the closed state provides a higher density. EP and sintering in the closed state (figure 1, columns 4) leads to the highest density among the investigated CM up to 2300 and 2395 kg/m³.

![Figure 1. Density of PTFE-aluminum CM: 1 - SP without sintering; 2 - SP with sintering in a free state; 3 - SP with sintering in the closed state; 4 - EP with sintering in the closed state.](image)

The structures of produced CM (figure 2) consist of evenly distributed aluminum particles in the polymer volume. The microstructures of the CM produced by the SP with sintering in the free state show a significant amount of voids formed because of deposition of aluminum particles from the polymer during polishing of the microsection, which is absent in CM produced by explosive pressing. This confirms that the best adhesion of aluminum particles to the polymer is achieved by the EP.
Thermal conductivity of PTFE based CM increases with an increase of aluminum content. Sintering in the free state reduces the thermal conductivity of PTFE based CM by 7-14%, and sintering in the closed increases it by 7-25%. CM, produced by EP and sintered in the closed state, have a 22-48% higher thermal conductivity than CM, produced by SP with sintering in the closed state.

Studies of the thermal expansion of the CM (figure 3) showed that the curves have a characteristic jump at temperatures $t_1$-$t_2$, caused by the melting of the crystalline phase of PTFE ($t_m = 341^\circ\text{C}$ before sintering and $t_m = 327^\circ\text{C}$ after sintering). In the temperature range below $t_1$ (table), a slight increase in deformation occurs due to the low thermal mobility of the macromolecules and the stable state of the PTFE crystalline phase. Above $t_2$ there is a uniform growth of deformations due to the misorientation of PTFE macromolecules in the crystallites, their melting and the increase in thermal motion.

**Figure 2.** Microstructure of PTFE filled with 10% (a) and 30% (b, c) of aluminum after: a - SP with sintering in the closed state; b - SP with sintering in the free state; c - EP with sintering in the closed state.

**Figure 3.** Thermal conductivity of PTFE filled with 10% and 30% aluminum: 1 - SP, without sintering; 2 - SP, with sintering in a free state; 3 - SP, with sintering in the closed state; 4 - EP with sintering in an ampoule.

**Figure 4.** Correlation between the thermal expansion of PTFE filled with 10% (a) and 30% (b) aluminum and the temperature: 1 - SP, without sintering; 2 - SP, with sintering in a free state; 3 - SP, with sintering in the closed state; 4 - EP with sintering in an ampoule.
It should be noted that in the CM after SP, without sintering and with sintering in the free state with an increase in the aluminum content from 10 to 30%, the transition temperatures practically do not change (table), and after EP and SP with sintering in the closed state, there is a 6-7% decrease in $t_1$, but it still doesn’t change $t_2$.

Thermal deformations $e_1$, occurring at $t_1$, are not as affected by the method of production as the deformations $e_2$ at $t_2$. Sintering of CM in the free state after SP leads to a decrease of $e_2$ by 3-8%, and sintering in the closed state either does not change $e_2$ at 10% aluminum content, or leads to a 7% decrease at 30% aluminum content. Sintering of the samples in the closed state after SP leads to an insignificant decrease of $t_1$ (3-5°C), in comparison with sintering in the free state. After EP and sintering in the closed state, regardless of the aluminum content, CM have $t_1$ higher by 25°C, and $t_2$ higher by 15°C than the same ones after the SP. After EP and sintering in the closed state, the deformations are practically the same as those after SP and sintering in the closed state, but $e_2$ is twice lower for CM with 30% aluminum, due to a smaller amount of polymer than in CM with 10% aluminum.

| Concentration, (%) | Production method | Sintering | $t_1$(°C) | $e_1$(%) | $t_2$(°C) | $e_2$(%) |
|-------------------|------------------|-----------|-----------|----------|-----------|----------|
| 10                | SP               | none      | 338       | 5        | 350       | 18       |
| 10                | SP               | f.s.\(^a\) | 320       | 6        | 335       | 10       |
| 10                | SP               | c.s.\(^b\) | 317       | 13       | 333       | 18       |
| 10                | EP               | c.s.\(^b\) | 342       | 3        | 348       | 17       |
| 30                | SP               | none      | 339       | 4        | 349       | 15       |
| 30                | SP               | f.s.\(^a\) | 321       | 8        | 334       | 12       |
| 30                | SP               | c.s.\(^b\) | 311       | 6        | 330       | 8        |
| 30                | EP               | c.s.\(^b\) | 335       | 4        | 346       | 7        |

\(^a\) sintering in the free state  
\(^b\) sintering in the closed state

The decrease in density and thermal conductivity after sintering in the free state is associated with the amorphization of PTFE with the possible rupture of adhesive bonds between the polymer and the metal, which is accompanied by an increase in porosity. This is confirmed by studies of the microstructure, which found a large amount of voids due to the deposition of aluminum particles.

The high density and thermal conductivity of the CM obtained by EP with sintering in the closed state is better than in those produced in the static state, which indicates a stronger adhesion interaction, formed under epy fast-acting impact of explosive energy. At the same time, due to the strengthening an interphase zone can be formed between PTFE and aluminum, properties of which differ from the matrix.

With an increase in the aluminum content, the thermal expansion of the composites is mainly reduced due to a decrease in the volume of the polymer matrix, which has a large coefficient of thermal expansion, and an increase in the number of contacts between polymer matrix and the metal which restrain the movement of macromolecules.

Explosive pressing with sintering in the closed state is better than static one with sintering in both free and closed states because it provides a stronger adhesive interaction upon contact of phases, as a result, metal particles restrict the movement of macromolecules and prevent thermal expansion.

**Conclusion**

Thus, for the production of PTFE-aluminum CM with high thermal conductivity and the lowest thermal expansion during heating, it is necessary to use explosive pressing of CM containing an increased amount of metal particles with sintering in a closed state, as it provides better adhesive interaction.

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