LIFE SAFETY

Scientific article
UDC 622.276; DOI: 10.61260/2304-0130-2025-1-79-89

THE USE OF THERMOELECTRIC TEXTILES BASED ON p-n SEGMENTAL COAXIAL AEROGEL FOR FIREFIGHTER'S TURNOUT GARMENT

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Abstract. The possibilities of using thermoelectric textiles in firefighters' turnout garment, including for powering an autonomous early warning system, are shown. The process of coaxial wet forming of fiber in the core-shell segment of the p-n junction based on the method of continuous alternating coaxial wet corkscrew is described. Polyparaphenylene terephthalamide fibers with a core-shell segment of the p-n junction were used in the experiment. The electrical properties of thermoelectric fibers, as well as the stress-strain relationships of n-segment, p-segment, and p-n segmented thermoelectric fibers, and the temperature dependence of the Seebeck coefficient are studied.

It was determined that thermoelectric p-type and n-type fibers with the same number of individual fibers generated almost the same output voltage, which indicated the possibility of forming a fiber battery. A conclusion is made about the possibility of using thermoelectric fabrics based on thermoelectric aramid nanofibers for the manufacture of firefighters' combat clothing and thereby providing autonomous power to fire alarm sensors.

Key words: firefighters' turnout garment, coaxial wet weaving, thermoelectric fiber, segmented fibers, thermoelectric textiles

For citation: Kuzmina T.A., Lobova S.F. The use of thermoelectric textiles based on p-n segmental coaxial aerogel for firefighter's turnout garment // Supervisory activities and forensic examination in the security system. 2025. № 1. P. 79–89. DOI: 10.61260/2304-0130-2025-1-79-89.

Introduction

Turnout garmnet should be an effective protective barrier between firefighters and fire hazards (FH), as well as play a vital role in minimizing burns to a firefighter's skin from high temperatures, combustion products, or thermal radiation from flames and ensuring the safety of personnel during fire extinguishing or emergency recovery operations [1]. Aramid fiber, which is the most effective material for turnout garment, can undergo thermal decomposition when the temperature of the combustion products exceeds 500 °C, which leads to its failure and does not provide thermal protection for firefighters [2]. Therefore, it is relevant to choose effective strategies to protect firefighters from heat exposure during fire and rescue operations, in particular, in conditions of extremely high temperature and flame.

Currently, effective firefighter protection strategies are primarily classified as active and passive fire protection strategies [3, 4]. In general, the passive protection is aimed at improving the thermal insulation of turnout gear by increasing the layers and thickness, which, in turn, leads to an increase of it's weight, complicates heat dissipation and worsens moisture permeability. Active firefighter protection strategy provides, for example, a special sensor integrated into garment, that allows the control of the temperature on its surface in case of fire. Such system makes it possible to provide early warning about the possibility of thermal decomposition of the garment [4]. Thus, firefighters can move to a safe distance and prevent possible damage to turnout gear, thereby ensuring their safety. This active concept of firefighter combat clothing was first described in [5] and attracted increased interest from researchers in the field of firefighter safety.

Currently, experts mainly study sensors which detect changes in resistance, based mostly on the use of graphene oxide and other semiconductor materials. This solution allows for a one-time early detection of the critical impact of FH on turnout garmnet, even in conditions of high humidity [6]. Semiconductor-based materials will make it possible to use a similar but reversible dependence of resistance on exposure to high-temperature combustion products (>500 °C) or thermal radiation (>1,5 kW/m^2) to trigger a warning of the critical impact of HF on a firefighter. Existing resistant fire alarm sensors require external electrical power sources, which do not always meet the needs of the service for a sufficiently long period [7]. Meanwhile, problems arise not only when they are integrated into combat clothing, but also when the complexity of the fire alarm system increases, which makes it more unstable, especially in hazardous conditions. The solution to the problem would be to create a wearable temperature sensor without an external power source.

The use of thermoelectric textiles (TET) has promising prospects in solving the above-mentioned problem of the production of wearable temperature sensors with autonomous power by miniaturizing them [8]. Compared to thermistors, TET-based sensors can directly convert fire heat into electrical energy and, accordingly, initiate a fire alarm system and alarm without an external power source [9]. However, the most difficult task is related to the development of technology nessecary for the creation of alternating p-n junctions in the productione of TET. At the same time, it is important to preserve such properties of TET as dynamic pliability of the surface, breathability, washability and flexibility.

So far, sequences of alternating p-n junctions on TET segmented fibers have been produced by coating, dipping, or spraying on conventional fibers with alternating such layers. However, the instability of the protective layer is observed and, as a result, its possible abrasion during prolonged mechanical friction and deformation caused by the combat work of a firefighter [4]. In contrast to the above approach, coaxial wet weaving is an effective way to form a sequence of alternating p-n junctions. Fibers with a protective shell structure provide the required mechanical and technical characteristics of TET. Such a TET structure involves the creation of sequentially connected p-n junctions along the fibers by means of weaving, which optimizes its thermoelectric characteristics [10].

Thus, the task of practical implementation of an effective firefighter protection strategy using the technology of manufacturing self-powered fire alarm sensors based on coaxial aerogel fibers with p-n junction segments arises.

Research methods

The authors of [5] used for the experiment individual polyparaphenylene terephthalamide fibers made using coaxial wet molding technology on a heart-shell segment of the p-n junction with a length of more than 1,200 mm, as well as fragments of TET with a size of at least 50 × 50 mm formed on the same basis.

In the manufacture of such a material, the deprotonation method was used. Weaving additives were prepared for the treatment of aramid fibers in the form of a special solution: 1,5 g of potassium hydroxide and the same amount of aramid fiber powder were added to a vessel with 3 ml of distilled water and 80 ml of dimethyl sulfoxide, followed by stirring for a week in a magnetic field. After that, a viscous dark red suspension with a concentration of 18 mg/ml is obtained. Thus, 0,2 g of montmorillonite was obtained, which was gradually added to 1 ml of dimethyl sulfoxide, and the resulting suspension was mechanically stirred at 1,000 rpm for half an hour to obtain a homogeneous dispersion. Finally, the resulting dispersion (1 ml) was mixed with the prepared suspension (25 ml), thus obtaining spinning additives for wet spinning [5].

Preparation for the formation of p-n junctions involves the gradual addition of 1 g of Ti_3AlC_2 powder into a teflon container with 20 ml of potassium hydroxide and 1,6 g of LiF and stirring in a constant magnetic field for 36 hours at room temperature. After that, the resulting product was rinsed repeatedly with distilled water and treated with ultrasound for three hours.

Next, the product was added to an aqueous solution of sericin (0,02 g/ml) and mechanically mixed for half an hour, achieving the formation of a homogeneous dispersion in the form of a weaving mass of n-segmented thermoelectric fibers.

The dispersion of single-walled carbon nanotubes (purity > 50 %, diameter < 2 nm and average length 5–30 microns) in a 1:1 mass ratio for the production of spinning additives such as p-type spinning dopes as other basic materials was obtained by oxidation in a mixture of sulfuric acid and nitric acid, which was supposed to improve conductivity and dispersibility additives.

To obtain type-p weaving additives of, 0,1 g of Ti_3AlC_2 powder was added to a mixture of sulfuric acid and nitric acid (3:1 by volume) and continuously mixed for 48 hours. The acid-treated product was then repeatedly washed with deionized water by centrifugation at 8,000 rpm to obtain a homogeneous suspension (50 mg/ml). The resulting suspension was mixed with layered lateral structures based on $Ti_3C_2T_x$ type with a 1:1 mass ratio as the additive for wet weaving thermoelectric (TE) fibers of the TET p segment was pressed [7, 11].

The process of coaxial wet forming of fiber with a core-shell segment of the p-n junction involves the use of a continuous alternating coaxial wet corkscrew method. This method involves the use of a special coaxial needle, which consists of an external needle (15 g, inner diameter: 1,4 mm) and an internal needle (22 g, inner diameter: 0,4 mm) (Fig. 1).

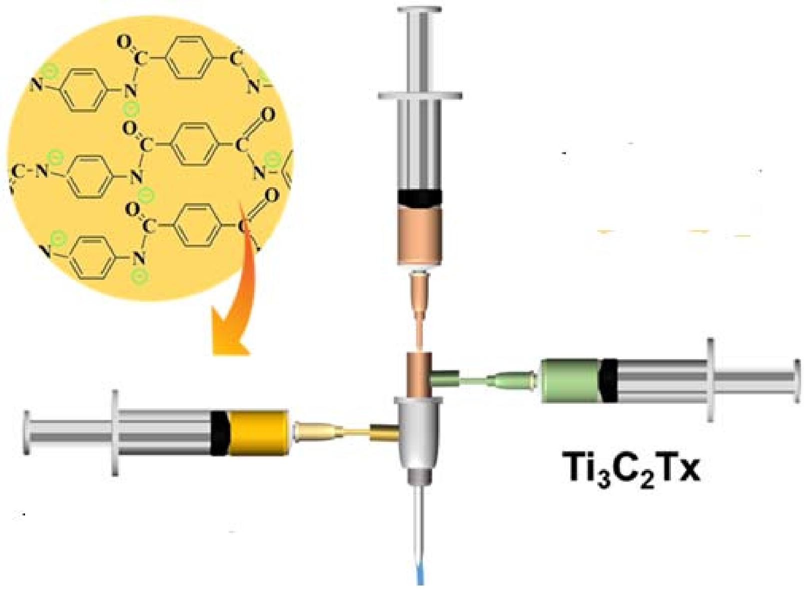

Fig. 1. **Diagram of the coaxial wet weaving process**

Molding materials were inserted into the outer needle. The weaving additives were pumped one after another into the inner needles using separate syringe pumps. The powders for forming the shell and core were extruded into a water-coagulation bath with a 2 % ammonium chloride solution at speeds of 300 and 150 µl/min, respectively. The constant coefficient of elongation during coaxial spinning was maintained at approximately 1,1. Then the formed fibers were soaked in a 50 % aqueous solution of tert-butyl alcohol until some of the water was removed. Next, the fibers were wound onto a winding coil and cooled on p-n junctions on the core-shell segments of the fiber (fig. 2).

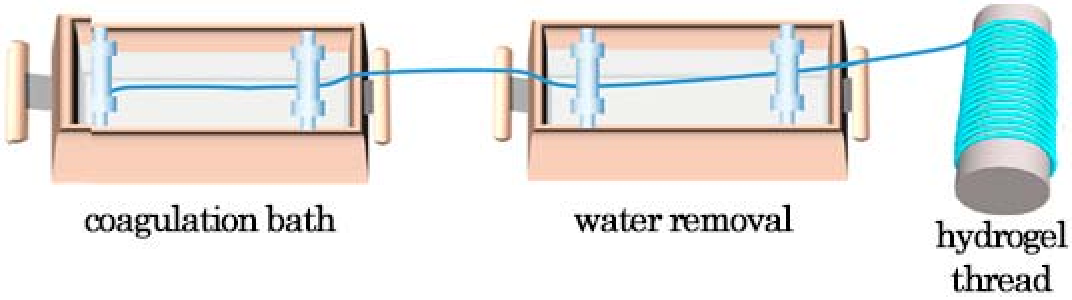

Fig. 2. **The core-shell fiber processing process**

The distance between the p-n junctions formed on the thermoelectric fiber was 1,2 cm, and the connection between them was made by silver nanowires (Ag NWs, of purity > 99,5 %, diameter 50 nm and average length 100 microns). The average length of the electrical connection between two adjacent TET fibers was 2 mm.

The electrical properties of the TE fibers were evaluated using a four-probe resistivity meter. The mechanical properties were investigated on an Instron 3365 testing machine at a tensile loading rate of 5 mm per minute. The behavior of fibers during thermal decomposition was evaluated using a STA 6000 thermogravimetric analyzer with a scanning speed of 10 °C per minute [12]. At the same time, the electrically conductive characteristics of TE fibers were studied using a system for determining the Seebeck coefficient and resistivity. The Dongguan Daxian millivoltmeter was used to record the generated output voltage signal from TE fibers with segmented p-n junctions.

The results of the study and their discussion

Based on the possibility of practical application, fire resistance is an important indicator for TET based on TE fibers with segmented p-n junctions as a material for the manufacture of turnout gear.

The vertical combustion test was carried out by researchers [9] in the process of visual assessment of the fire resistance of TET with TE fibers segmented by p-n junctions. A segment of TE fiber without montmorillonite immediately caught fire as soon as it came into contact with an open flame, and burned out within three seconds.

On the contrary, the segmented TE fiber did not ignite and retained its shape after direct contact with an open flame for five seconds, confirming that montmorillonite increases the fire resistance of p-n segmented TE fibers.

The mechanical characteristics of the TET are an important parameter determining the possibility of placing temperature sensors on combat clothing. Figure 3 shows graphical dependences of the tensile stress-strain of the p-segment, n-segment, and alternating p-n for segmented TE fibers [9].

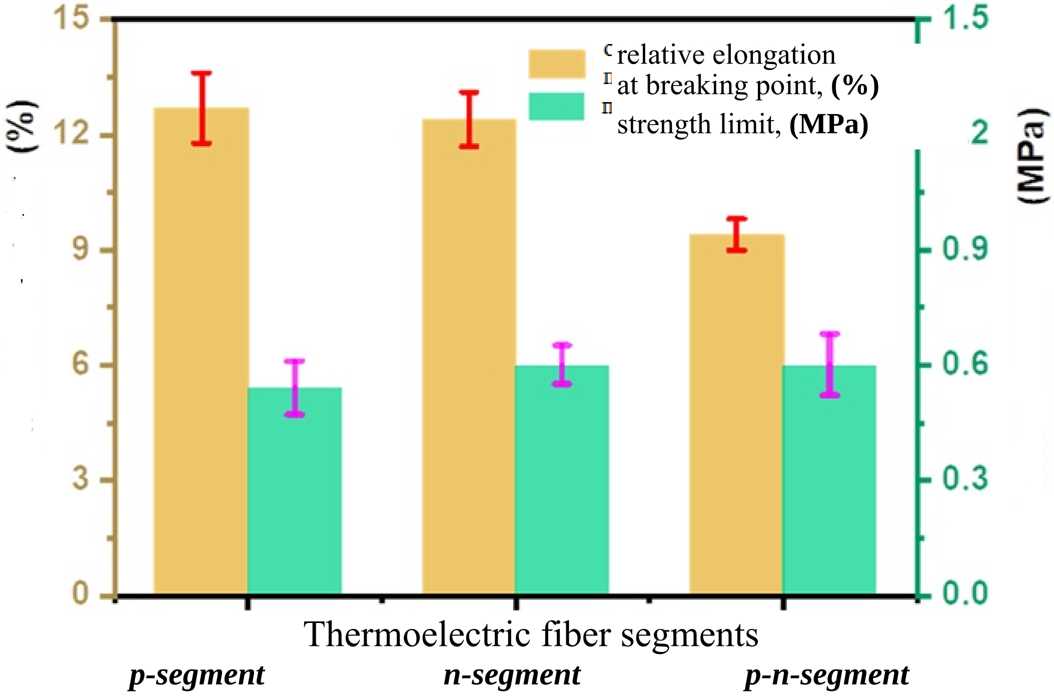

Fig. 3. **Mechanical properties of segmented TE fibers**

Figure 4 shows the respective measurement results of the p- and n-segments of the TE fiber.

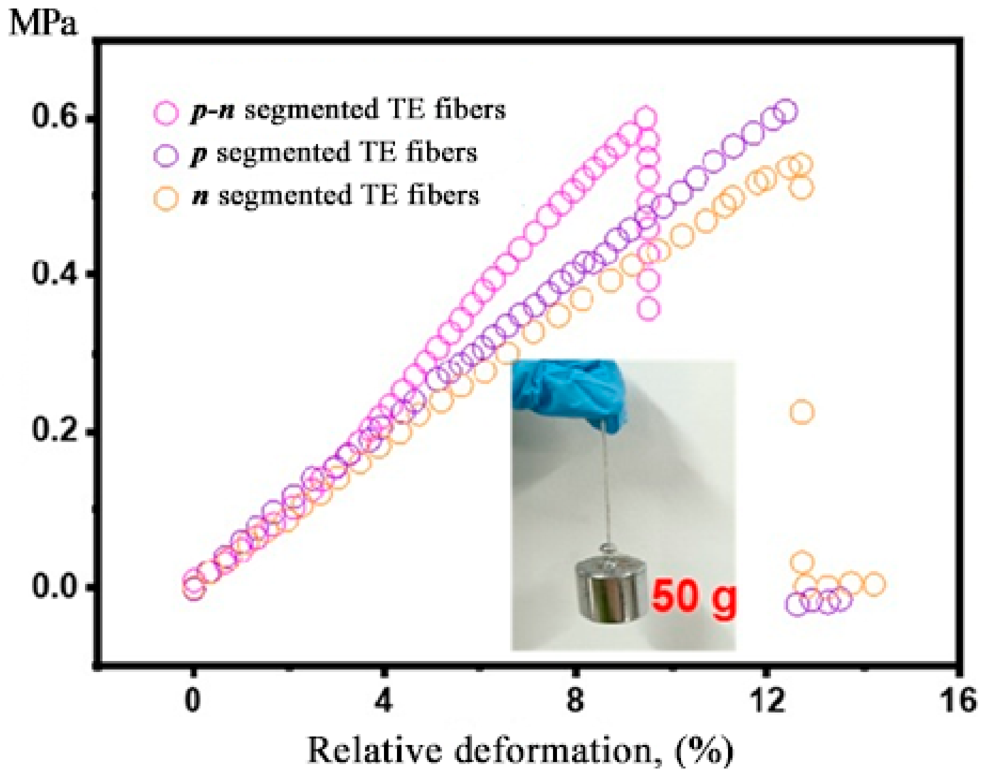

Fig. 4. **Stress-strain dependences of n-segment, p-segment, and p-n segmented TE fibers**

The obtained measurement results allowed us to conclude that the p-segments and n-segments of TE fibers allow a maximum elongation of 12,4 % and 12,7 % at tensile stresses of 0,54 and 0,6 MPa, respectively. In contrast, p-n segmented TE fiber showed a similar tensile strength of 0,56 MPa and elongation at break of 9,4 %.

In addition, the characteristics (electrical resistance, diameter, tensile strength limit, porosity, viscosity, flexibility) of p-n segmented TE fibers were additionally investigated for the possibility of their use for the manufacture of firefighters' combat clothing by comparing them with those described in the works [2, 5, 7, 9, 13] aerogel fiber (fig. 5).

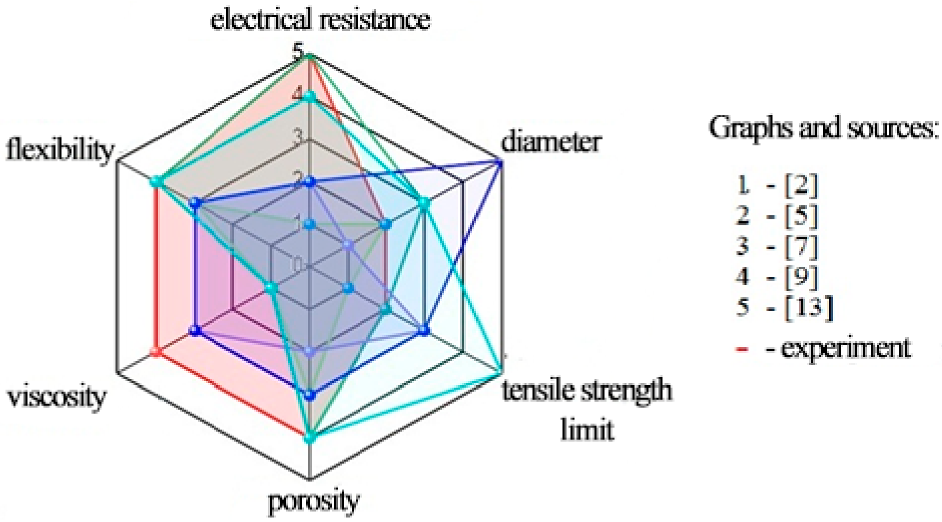

Fig. 5. **Comparative diagram of the main characteristics of p-n segmented TE and aerogel fibers**

As shown in fig. 6, the value of the Seebeck coefficient was negative in the range of 200–350 °C, which means that electrons are the main carriers of electric charge.

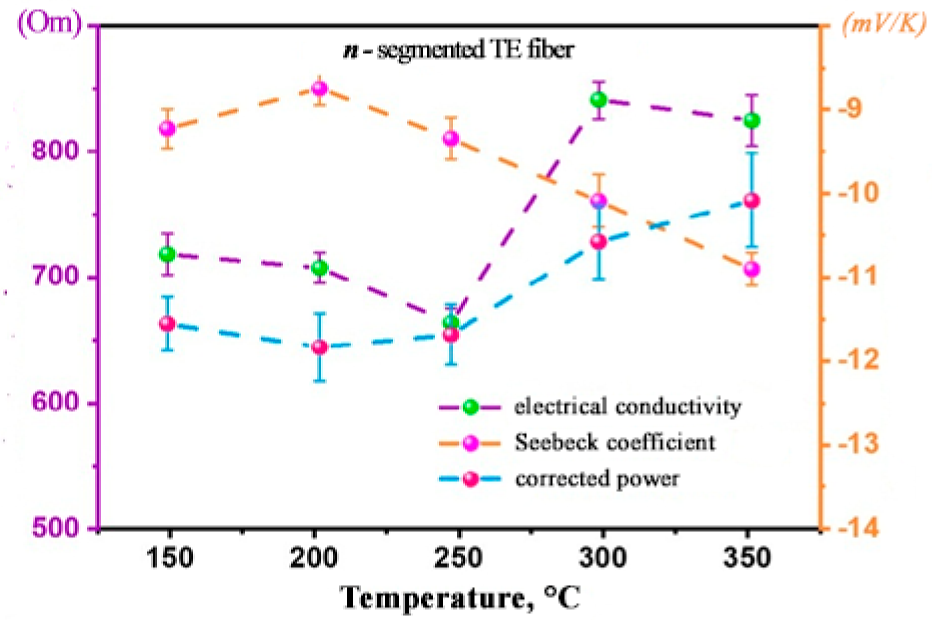

Fig. 6. **Electrical characteristics of n-segmented TE fiber**

The value of the Seebeck coefficient in the n-segment of the TE fiber decreased as it warmed up, then gradually increased, and the electrical conductivity showed the opposite trend, demonstrating typical metal-like behavior.

With the addition of acid-treated carbon nanotube particles to the suspension in the temperature range of 150–350 °C, the value of the Seebeck coefficient changed to positive. This confirms the presence of p-type carriers in the core of the p-segmented TE fiber (fig. 7).

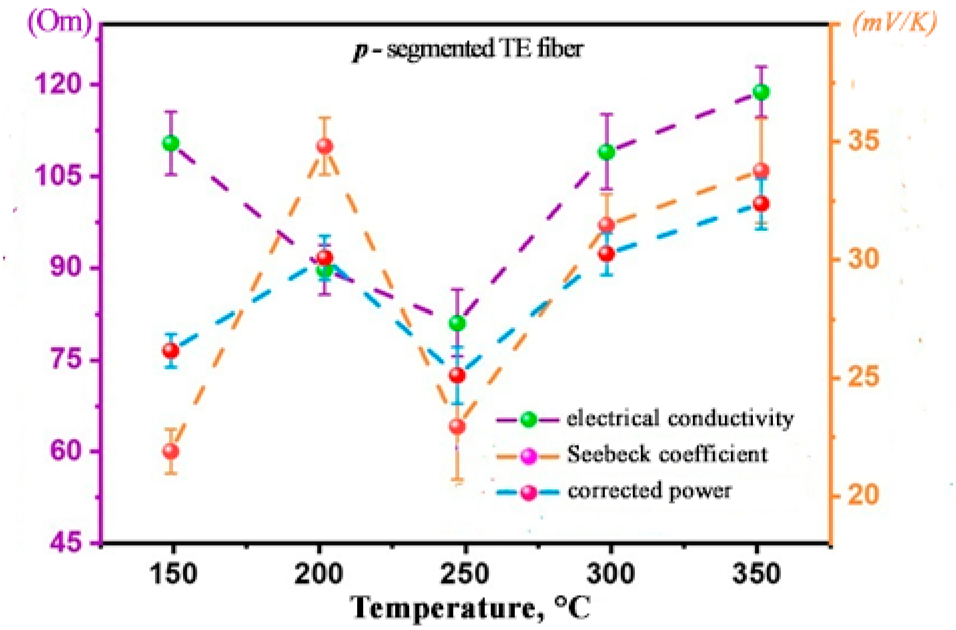

Fig. 6. **Electrical characteristics of p-segmented TE fiber**

The temperature dependence of the reduced power of a p-segmented TE fiber in the range of 200–250 °C practically reiterates the temperature dependence of the Seebeck coefficient: firstly decreasing and increasing later.

The electrical resistance of a circuit of two pairs of p-n segmented TE segments t a temperature of 20 °C was 23,76 Om.

As shown in fig. 8, the number of fibers affects the output voltage removed from p-type TE fibers and n-type TE fibers in the temperature range of 50–400 °C, which is relevant for turnout gear.

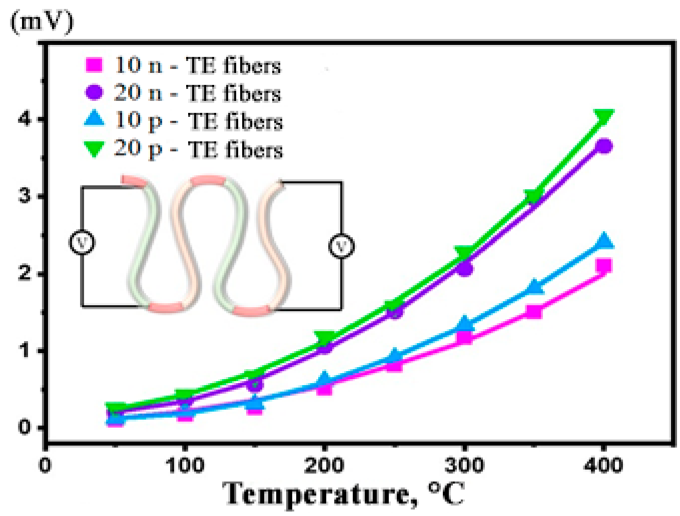

Fig. 8. **Output voltage of different number of fibers of type p or n at different temperatures**

The experimental results showed that the output voltage increased roughly linearly along with increasing temperature, and the output voltage of the p-type TE fibers (consisting of 20 individual fibers) was almost twice as high as that of the same TE fiber containing 10 individual fibers. In particular, the output voltage of the p-type fibers containing 10 individual fibers was 2,31 mV, and that of the p-type fiber consisting of 20 individual fibers was 4,17 mV at the same temperature of 400 °C. Meanwhile, p-type TE fiber and n-type TE fiber with the same number of individual fibers generated almost the same output voltage, the value of which indicated the prospect of forming a battery of segmented p-n TE fibers.

Figure 9 shows the results of measurements of the output voltage on TE fibers with a different number of p-n segments at different temperatures.

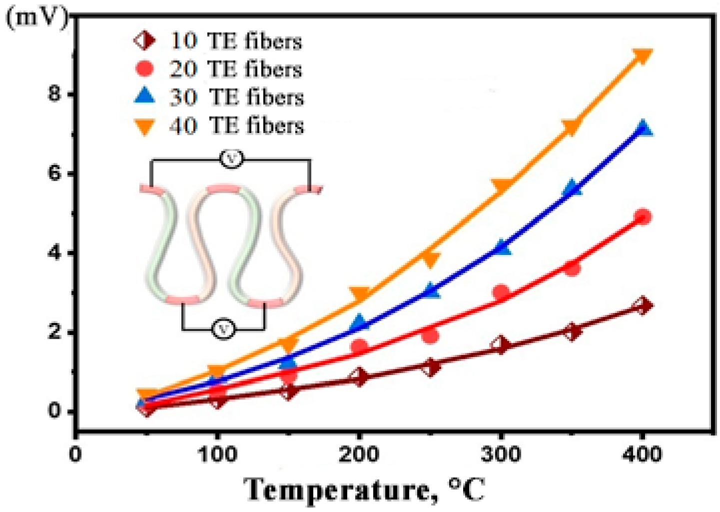

Fig. 9. **Open-circuit voltages of p-n segmented TE fibers at different temperatures**

For p-n segmented TE fibers, the length of which increased from 10 to 40 p-n pairs, an increase in the output voltage was observed from 2,68 mV to 9,01 mV at a temperature of 400 °C, which is typical for traditional thermoelectric materials [10].

The process of investigating the repeatability and stability of power generation involved five cycles of alternating heating (400 °C) and cooling (20 °C) TE with 20 pairs of p-n segments (fig. 10).

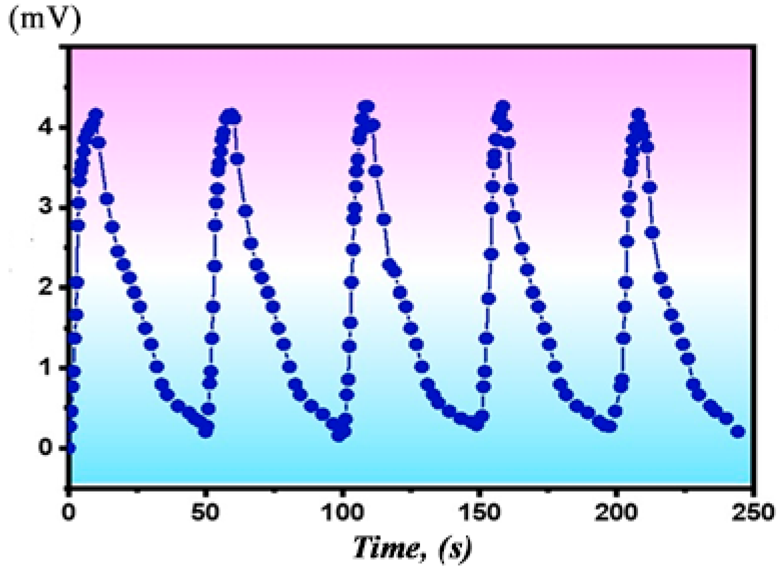

Fig. 10. **Output voltage on 20 pairs of p-n segmented TE fibers for 5 cycles: heating up to 400 °C and cooling down to 20 °C**

It was determined that the highest output voltage on TE fibers with 20 pairs of p-n segments was observed at a temperature of 400 °C and remained unchanged at about 4,25 mV during five heating and cooling cycles.

Considering that during the combat work of a firefighter, his clothes inevitably bend when worn, the resistance to change of the p-n segments of TE fibers $(R\text{-}R_o)/R_o$ (R_o and R are the resistance before and after bending, respectively), and the output voltage was studied at various bending angles from 0 to 180° at a temperature of 20 °S (fig. 11).

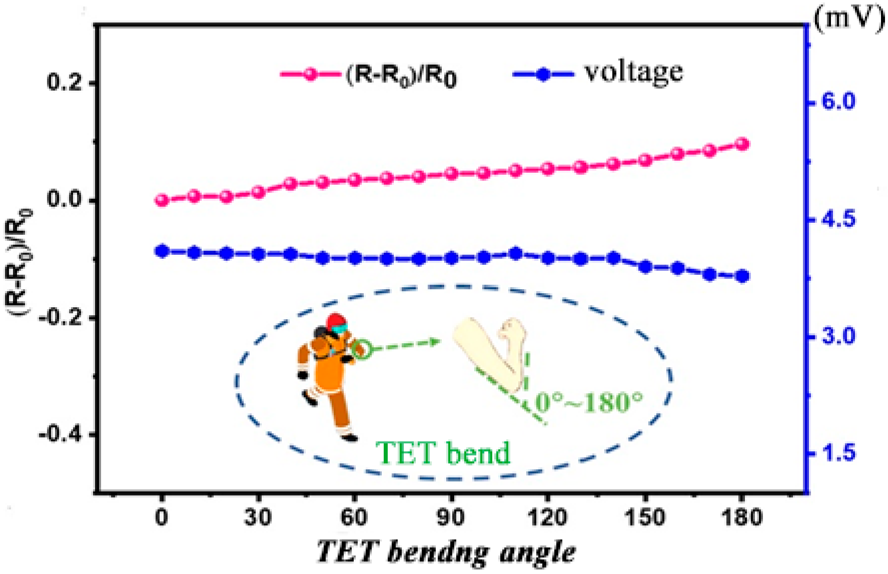

Fig. 11. **Change of resistance and output voltage at different bending angles for TET**

The measurement results suggest that the range of resistance variation was less than 9,6 %, and the maximum level of output voltage loss on the p-n segments of the TE fibers was 7,8 %.

To further study the durability of the p-n segment of TE fibers, changes in relative resistance (R-R$_0$)R$_0$ and output voltage (V-V$_0$)/V$_0$ (V$_0$ and V) were measured before and after bending, respectively after 200 cycles, bending by 150° (fig. 12)

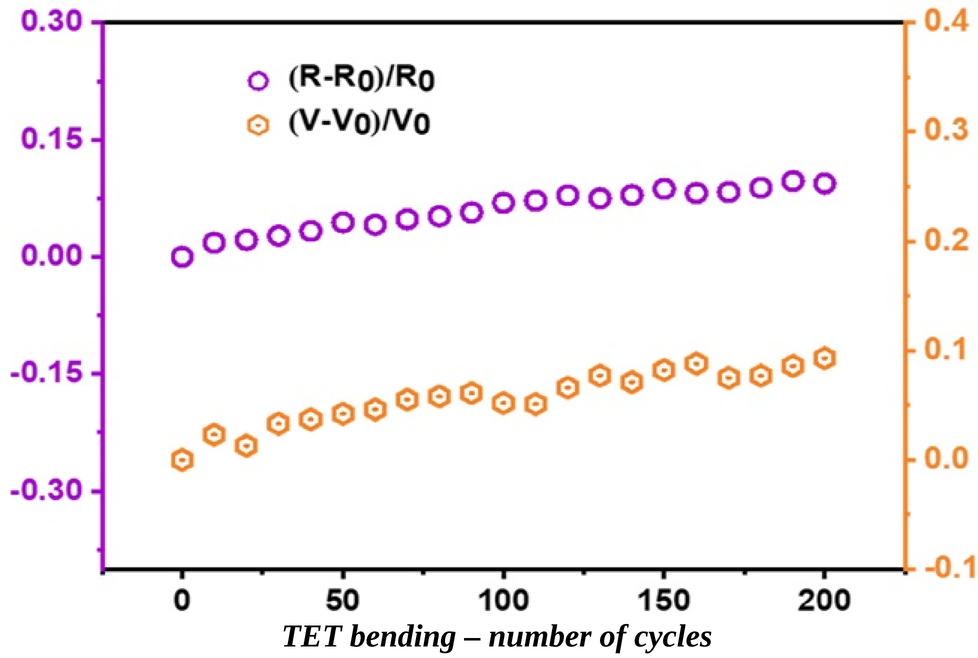

Fig. 12. **Effect of TE fibers bending cycles on resistance and stress values at a bending angle of 150°C with 20 pairs of p-n segments**

The measurement results showed that the maximum changes in voltage and resistance were 9,7 % and 9,3 % after 200-fold flexion-extension of the TET, respectively.

Conclusion

The possibility of using TET based on aramid nanofibers for the manufacture of firefighters' turnout garment and thereby providing autonomous power to fire alarm sensors was confirmed during the experiments conducted [5, 9].

The analysis of the mechanical properties of p-n segmented thermoelectric fibers suggests that the conductivity characteristics (class 5), viscosity (class 4) and flexibility (class 4) make it practically plausible to place resistive thermal sensors on firefighter turnout gear.

The mechanism of electric energy generation on p-n segmented TE fibers is based on the temperature difference of different segments.

The number of fibers in the TET affects the output voltage removed from the p-type and n-type TE fibers in the temperature range of 50–400 °C, which is relevant for firefighting.

It can be assumed that the stability of the resistance and output voltage on the p-n segments of the TE aramid nanofibers during bending of the TET were mainly due to the formed protective shell.

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Information about the article: submitted for editing: 02.02.2025; accepted for publishing: 03.03.2025

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