Nano-sized Al-Ni energetic powder material for heat release element of thermoelectric device

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Abstract. In this paper, a method of fabrication of an Al-Ni powder energetic material with a 90-100 nm particles is proposed and experimental results of a study of its properties are presented. High values of specific energy and the rate of its release make it possible to use this material as an heat release element in thermoelectric power generation devices. It has been demonstrated experimentally that it is possible to maintain a voltage value higher than 1 V for 45 seconds as a result of combustion of a 3 gram Al-Ni sample that using a simple DC-DC converter will allow charging supercapacitors or accumulators.

1. Introduction
In recent years scientists are focused on development of environmentally friendly energy sources capable of operating under extreme conditions such as Far North and Arctic regions. Thermoelectric generators convert heat from various sources into electrical current. They are highly reliable due to the simplicity of construction and the absence of moving parts [1]. Currently, they are used in conjunction with various sources of heat: from the heat of the human body [4], solar energy [2], ending with radioisotope fuel [3]. However, the listed heat sources are not without shortcomings - they are periodic in time, ineffective and environmentally and biologically unsafe. In this regard, the development of new sources of heat is an urgent task.

Thermites are a well-studied class of materials with a centuries-old history [5] and up to now they have been used for various surfaces joining [6]: from railroad rails to microelectronic components [7]. These energy materials are able to maintain in their volume a self-propagating exothermic reaction after primary initiation, resulting in a significant amount of heat released.

The most common thermite mixtures are the metal-oxide pairs, for example, Al-Fe$_3$O$_4$, Al-CuO and Al-Cu$_2$O, as well as bimetallic pairs: Al-Pt, Al-Ni, Al-Zr. The last of these are distinguished by the absence of gas evolution in the combustion process while maintaining a relatively high specific energy density. Due to this, a thermoelectric device based on them (a schematic image of which is shown in figure 1) consisting of a source of heat generation, a thermoelectric generator and an accumulation device of generated electric energy can be created.
Figure 1. Schematic representation of the construction of a thermoelectric device

The state-of-the-art technology allows the production of powder materials with a particle size of less than 100 nm, which makes it possible to create energy materials with improved characteristics: lower initiation energy and faster propagation velocity of the wave front [8].

In the present article, a method of fabrication of heat generation element based on nanosize commercially available aluminum and nickel powder materials is proposed. The results of experimental studies of energy composites using DSC and high-speed video recording are presented, as well as the output characteristics of a thermoelectric generator under the influence of the investigated aluminum-nickel energy material.

2. Experiments and results

The initial aluminum and nickel powders with particles sizes from 70 to 100 nm were obtained from LLC (APT) Advanced Powder Technologies. Energetic composite was prepared by mixing the components in an Al: Ni ratio of 50:50 at% in an ultrasonic bath for 2 hours. The hexane was added to the mixture of the initial powders as process control agent for better mixing, after that it was removed by means of a rotary evaporator. Finally mixtures were pressed without binder component in the form of a disk 25 mm in diameter with a porosity of 0.53 by means of a hydraulic press AE&T T61220M.

The study of thermal effects in compressed materials by differential scanning calorimetry was carried out using TA Instruments Q600 equipment. A 10 mg sample was placed in a ceramic (Al₂O₃) crucible and heated at 10 °C/min rate from room temperature to 800 °C in an argon flow (50 ml/min). The absolute value of the thermal effect was determined by the integration of the DSC curve over time in the region of the main exothermic peaks. The calculated value was about 792 J / g, which is lower than the theoretical value, but it may be due to the incompleteness of the chemical reaction between aluminum and nickel, and also due to the presence of an oxide layer on the surface of the aluminum particles.

Measurement of the reaction front propagation velocity after electrical initiation in pressed samples was carried out using high-speed video at a speed of 10,000 fps. The initiation of wave combustion was controlled with the help of two tungsten probes, located at a distance of 2-4 mm. For the initiation, a short-time power supply was used. The numerical value of the front velocity was defined as the ratio of the distance traveled by the front to the time during which this process occurred. During the combustion, the front of the chemical interaction was clearly visible and spread throughout the sample area at a velocity of 0.056 m / s, which is shown in Figure 2.
To study the output characteristics of the TEG under the influence of the heat-release element based on the Al-Ni energetic powder material, a special stand was designed. The thermoelectric generator TMG-127-1.4-1.5 was installed with a cold side on an aluminum radiator. On the cold side the compacted energy material in the form of a disk 25 mm in diameter and not more than 5 mm thick was placed. The sample weight ranged from 0.3 to 3 grams. For a more uniform heat distribution and to avoid thermal shock, a copper plate with dimensions 40 * 40 * 0.6 mm was placed between the energy material and the TEG. To improve thermal contacts, thermal paste was applied to both sides of the TEG. To avoid heat loss, the energy material and TEG were covered with a heat-insulating material based on gypsum. The TEG contacts were connected to the measuring circuit with a Keithley 2700 multimeter in series or in parallel to measure the output characteristics (Uoc, Isc and U, I without load and with load, respectively) depending on the fixed value.

Figure 3 shows the graphs of the change in the output voltage of the TEG (with 1.8 Ohms load) in the combustion process of energetic materials of different masses. In all cases, the graphs had a similar shape - rapid growth to a maximum value and a slow decline. The maximum value of the voltage and current were 2 V and 0.8 A respectively for a 3 grams sample and it was achieved in 10 seconds. The rate of increase in the magnitude of the voltage was the same in all experiments, and it is obviously determined by the thermal resistance of the TEG.

From a practical point of view, it is important to note that the voltage above 1 V was maintained for 45 seconds, i.e. using a simple DC-DC converter it is possible to charge electrochemical capacitors.
The efficiency of the thermoelectric device was calculated by the formula 1, where $Q_g$ - is the value of the generated by TEG electric energy (the integration of the power function over time), and $Q_m$ - is the specific value of the energy released for the Al-Ni energetic material, measured with DSC. The calculated values are shown in Table 1.

$$\eta = \frac{Q_g}{Q_m} \times 100\% \tag{1}$$

**Table 1.** The calculated value of the generated energy and the efficiency coefficient for different masses of the energetic material

| Weight (g) | Energy (J) | Coefficient of efficiency (%) |
|------------|------------|-------------------------------|
| 0.3        | 0.66       | 0.3                           |
| 1          | 14.82      | 1.9                           |
| 3          | 81.55      | 3.4                           |

Dependence of the coefficient of efficiency on the mass of the element of heat generation was found. It can be explained in terms of heat loss due to dissipation in thermal insulation. The absolute value of losses is the same in all cases, but for a case with a low mass of energetic material, it will constitute a significant fraction of the total amount of heat released. It is expected that with a further increase in mass, the efficiency will go to saturation. Nevertheless, the maximum efficiency will be limited by the efficiency of the thermoelectric generator, which currently is no more than 10%.

### 3. Conclusion

In the article, a thermoelectric device that converts the heat generated as a result of the combustion of a thermite-like Al-Ni energetic material was first time considered. The ability to maintain the output voltage of the TEG above 1 V for 45 seconds has been demonstrated that using a simple DC-DC converter will allow charging of batteries or supercapacitors or feeding other electronic components and devices. The value of the output voltage of 1 V was reached in only 2.5 seconds, which will allow using this type of device in extreme situations, when it is necessary to quickly provide power to the emergency notification system.

Further increase in the efficiency of the device (the maximum achieved was 3.4%) is possible due to optimization of the thermal insulation system to reduce heat losses. In addition, it is necessary to optimize the energy material in terms of the initiation energy, since the material considered in this article is characterized by a relatively high value of the initiation energy. The solution to this problem can be the use of various additives that stimulate the combustion process.

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