Using the novel capable of SHS-reaction multilayer nanostructured material for soldering of lead-zirconate-titanate piezoceramic elements

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Abstract. A novel integrated approach of solving the problem of the high-quality electrically conductive fastening of lead-zirconate-titanate piezoelectric elements is proposed. The essence of the method is that the specially created reactive multilayer material is used both as an electrode and as a solder. The mentioned reactive material is deposited directly onto the piezoelements surfaces by means of vacuum magnetron sputtering.

1. Introduction

Throughout the 20th century, the application field of materials with piezoelectric properties was steadily expanding. Currently, the use of piezoceramic elements in modern electronics is becoming more and more widely spread: its areas include radio electronics, hydroacoustics, ultrasound, measuring and medical equipment, piezoelectric motors, probe microscopy and others. The field of technologies for creating such elements is also expanding: from thick piezoceramics to multilayer nanostructured thin piezo films. The solutions of a number of applied tasks in the field of piezoelements still need improvement of the production methods and approaches. One of these acute problems is the creation of stack piezo transducers.

The output characteristics of the piezoelectric element itself may often be insufficient for creation of a single element-based transducer. So, assemblies of piezoelectric elements are used in, for example, receiving and transmitting hydroacoustic modules. The whole system of interconnected elements should work as a whole. The geometry of the system allows to achieve the optimal for its performance piezoelectric effect.

When designing the geometry of the system, many factors are taken into account: the material of each piezoelectric element, its resonant frequency, sensitivity, operating frequency range, relative position of the applied to the piezo element force vector F, polarization P, and electric field E [1]. Thus, the same piezoelectric element can be used in various integral stack modules differing in spatial energy-power structure [1]. For such converters, the physics of the processes occurring in them has not yet been fully studied. However, there are no doubts that the following factors are relevant to their output characteristics [2, 3, 4]: changes of the electrical capacitance between the electrodes, energy dissipation on the domain structures inside the module, the occurrence of parasitic oscillations in the piezoelement, and many more. Determining the contribution of each of these factors is a separate promising and necessary area of study. At the same time, in the complex of issues arising during the
integrated stack piezomodules assembling, the problem of high-quality electrically conductive fastening of the module elements takes an important place.

We suggest dividing the problem of the piezoelements fastening into two parts: 1. The problem of highly adhesive non-destructive metallization of piezoceramic elements; 2. The problem of implementing durable electrically conductive fastening of the piezo elements with reduced interface losses.

Several techniques are used in modern device fabrication for metallization of piezoelectric elements [5]. Currently, the most common metallization methods are high-temperature silver paste burn-in and deposition of silver-containing paste in microwave fields with megahertz-range frequencies [6, 7].

In this article we propose an alternative to the above methods of reducing the negative impact of electrical capacitance changes and the occurrence of parasitic amplitude-frequency characteristics at the interface of piezoelectric elements. We consider joining the piezoelements using a multilayer nanomaterial capable of demonstrating self-propagating high-temperature synthesis (SHS). The material was grown directly on the piezoelements by vacuum magnetron sputtering method.

2. Experimental Methods and Samples
The main idea of the proposed fastening method is to use the energy of the SHS process for soldering piezoelectric elements to each other.

Two types of piezoelectric elements made of lead zirconate-titanate were studied: PZT-19 and PZT-24 produced by Avrora-Elma company. All samples had been pre-polarized by the manufacturer, but had not been metallized. An attempt to assemble a two-element stack piezomodule was made in order to test the considered soldering technology. Thus, two types of sample devices were distinguished: one stack piezomodule from PZT-19 and the other from PZT-24.

Both PZT-19 and PZT-24 piezoceramic elements were metallized with the above-mentioned multilayer reactive structure using the vacuum magnetron sputtering method. This method showed the possibility of obtaining a metal electrode on the surface of the piezoelectric element at temperatures not exceeding 84 °C, which is well below the Curie point for selected samples. Thus, the thermal treatment influence on the electrical properties of the samples can be neglected.

After completing the metallization, a series of experiments were conducted revealing the advantages of the proposed method of piezoelements joining. The studies can be divided into two groups: 1. research of the multilayer SHS nanostructure itself; 2. investigation of the electrical and strength characteristics of the joint made by the realizing of SHS-reaction in the grown structure.

The first group includes consideration of the multilayer films’ internal and surface topography and its adhesive strength testing. The second part comprises obtaining the resonance characteristics of piezoceramic elements after the soldering, porosity measurement of the soldered joint and its climatic tests.

The internal topography of the structures was investigated by the SEM method using a TESCAN VEGA 3 electron microscope.

The adhesive strength of the deposited multilayer structure was experimentally determined by the scribing method. The main parameter of interest was the critical value of the applied to the needle load, at which the multilayer structure was removed from the surface of the piezoelement. The detailed descriptions of this conventional procedure can be found elsewhere [24-28].

After that a comparative assessment of the surface topography was made using a Profi-130 by Proton MIET, Ltd. profilometer.

After the proposed structure had been created on the sample surface, the process of degreasing was carried out according to the soldering of piezoelements specifications [8].

A special tooling was prepared for fixating the piezoelectric elements. It includes the main rod, a retainer, a coupling element (which also acts as a weighting) and a pressure meter. The elements were installed with opposite polarity relative to each other, then pressed with a load of about 1.5 kgf. A discharge voltage of 6.5 V was used to induce the SHS reaction.
Each stack of the transmitting and receiving module consists of two piezoceramic elements, either PZT-19 and or PZT-24 type. The reaction was launched at each junction of the elements one after another.

The study of solder joint porosity was performed by standard X-ray control of the compound in two profiles differing in the X-ray penetration depths. The void ratio was compared with such typical of joins produced by classical soldering in a furnace at a temperature of 230 °C using Sn96.5/Ag3/Cu0.5 solder. Also piezoceramic elements PZT-19 and PZT-24 were taken as control samples.

A special apparatus designed for obtaining the amplitude-frequency response «Censurka-M» was used for the measurement of the electrophysical parameters of the assembled piezoceramic stack as well as for determining the possible influence of the self-propagating high-temperature synthesis process on these parameters. The electrical characteristics of the unjoined elements had been obtained beforehand using the same apparatus.

Obtaining strength characteristics was carried out using the MFM1200 instrument. The set of trials included pull testing as well as shear, shock and vibration tests.

3. Results and Discussion

It is known that the temperature of a reactive material during the SHS-process is able to rise up to ca. 1500 °C in a fracture of a second. The SHS process itself is an exothermic chain reaction generating a heat wave with a front moving at speeds of 5 to 24 m/s.

However, with regard to piezoelements, the situation with the use of preforms of SHS material revealed a number of difficulties. The first of these was the negative effect of too much energy released on the adhesion of the metallization of elements.

As is known [8, 9], the reaction of the SHS material is able to warm up to temperatures of the order of 1500 °C in a split second. The SHS process itself is a chain exothermic reaction with a front of a heat wave moving at a speed of 5 to 24 m/s. The use of this feature of SHS materials can find its application in modern electronics, for example, this property can be utilized for soldering of two metal elements one to the other without damaging them.

However, the use of SHS-material preforms for soldering of piezoelements met certain difficulties. Firstly, the release of excess energy resulted in the deterioration of adhesive properties of the elements metallization layers (figure 1).

Secondly, using standard multilayer reactive foils for soldering led to the formation of spurious peaks in the frequency response of the assembled device (figure 1) [9].

We consider metallizing the piezoelements by growing the reactive SHS nanostructure directly on them by means of vacuum magnetron sputtering in order to overcome both mentioned difficulties. The proposed novel structure is characterized by ca. 2.7 times lower energy release density compared to
the previously investigated materials described in [9], and still this value is sufficient for the self-sustained reaction propagation. The energy reduction is achieved by introducing copper into the proposed reactive material, as well as by changing the molar ratio of the reacting elements.

The main challenge of the appropriate structure production was determining the sputtering regimes for each of the components in order to improve the adhesive properties as much as possible.

To determine the quantitative characteristic of adhesion, the work of adhesion value $W_a$ was considered - this is the work, taken per unit area, necessary for isothermal reversible separation of two condensed phases, which were previously brought into contact [10]. The following formula can be stated: $W_a = w \cdot N$, where $w$ denotes the average energy of a unit of adhesive bond, $N$ is the number of bonds per unit of the contact area. $N$ is determined by the contact area between the substrate (in our case it is the piezoelectric ceramics) and the adhesive (this is a Cr sublayer with Cu coating and the reactive multilayer structure deposited on the top of it).

Modelling of adhesion processes based on the classical adhesion theory [10] showed that when a 50 (or less) nm thick Cr or Ti sublayer is deposited onto the sample surface, the adhesion to this sublayer of the reactive SHS structure grown in the next stage will be significantly better than the adhesion of the same structures on pure ceramics.

We have developed and implemented our own method of growing an adhesive sublayer by means of vacuum magnetron sputtering. We used Cr and Ti sputtering targets and the process was carried out in two steps: at first a 10 nm thick Cr sublayer was deposited and then it was covered with a 50 nm thick Ti sublayer. The sputtering power was approximately 80 W, and it was performed at Ar atmosphere with pressure of about $7 \times 10^{-3}$ mbar. The vacuum chamber was opened for replacing the sputtering targets only after both adhesive sublayers had been deposited.

Then the reactive multilayer structure itself was created, also by vacuum magnetron sputtering using Al, Ni and Cu targets. It was performed in a single process, the bilayer thickness did not exceed 100 nm, the multilayer system was covered by a 7 μm thick Cu adhesive layer and the total thickness of the whole metallization layer reached approximately 50 μm. Finally, a 160 nm thick Cu film was deposited onto the structure as a top coat.

![Figure 2. Metallization profile of the PZT-19 and PZT-24 piezoelectric elements.](image)
It was not to remove the grown multilayer structure during the adhesion strength testing as the destruction or, at least, fracturing of the piezoceramic samples themselves was observed when the value of the load applied to the needle reached approximately 19 N. This force parameter corresponds to the mechanical strength limit declared by the manufacturer for PZT-19 and PZT-24. Based on the experimental results, it can be concluded that the adhesive strength of the structure deposited by magnetron sputtering is sufficiently high. This, in turn, allows the use of this method for obtaining a high-adhesive metallization of materials with similar physical characteristics to the considered in the present work samples (figure 2).

After creating such a structure, which is designed to be both the electrode for the piezoelectric element and the heat source for soldering the stack from these elements it is necessary to create a bonding solder layer. To do this, a thick (of the order of a dozen micrometres) Sn96.5/Ag3/Cu0.5 layer was deposited onto the above-mentioned Cu top coat by the chemical deposition method. This particular material was chosen as it is often used for «classical» soldering of piezoelements.

All in all, the thickness of the soldering coating of the samples obtained by the contact deposition method did not exceed 35 μm.

The surface topography was studied with a Profi-130 scanning profilometer, and the deviations were found to be no more than 3.1 micrometres which, with a total coating thickness of 30-35 microns, does not exceed 10 % of the latter. Such a smooth coating provides a uniform spreading of solder during heating and good wettability of the surface.

After the assembly of the stacks, the quality of the soldered seams was investigated by assessing the following parameters: longitudinal shear strength, single tear strength, single longitudinal impact strength and seam porosity. Moreover, the effect of the SHS reaction on piezoelectric parameters, namely, the resonant frequency F, the total capacitance of the stack C and the slope of the dielectric loss tg(δ) of the samples was experimentally studied. The results of the seam porosity measurements are given in figure3.

The results of the electrical parameters measurements for the piezoelements used for the devices fabrication are summarized in the Table 1. PZT19.1 and PZT19.3 rows contain the parameters of the PZT-19 samples before and after the fastening, correspondingly. Similarly, PZT24.2 data relate to PZT-24 sample before its soldering and PZT24.4 gives the parameters after the completion of the assembling. The data regarding the strength, temperature and electrochemical parameters of the seams are given in table 2.
Table 1. Changes in the resonance characteristics and other electrical parameters of the piezoceramic elements.

| Piezoelement | Cel, nF | $\delta$, % | $F_{r_{\text{max}}}$ | $F_{a_{\text{min}}}$ | $F_{a-\text{Fr}}$, kHz | $|Y_{\text{res}}|/|Y_{\text{ares}}|$ |
|--------------|--------|-------------|-----------------|----------------|-------------------|------------------|
| PZT 19.1     | 2.87   | 1.13        | 17.27           | 18.15          | 0.87              | 119.73           |
| PZT 24.2     | 2.87   | 1.30        | 17.23           | 18.10          | 0.87              | 104.30           |
| PZT 19.3     | 2.89   | 1.23        | 17.27           | 18.15          | 0.87              | 124.13           |
| PZT 24.4     | 2.87   | 1.18        | 17.30           | 18.17          | 0.88              | 122.21           |

Table 2. Strength and thermoelectric parameters of the soldered seams.

| $T_{\text{ad}}$, °C | $\sigma$, MPa | $\tau_{\text{mean}}$, MPa | $E$, GPa | $G$, GPa | $\mu$ |
|---------------------|---------------|--------------------------|----------|----------|-------|
| PZT-19              | 1450          | 48                       | 45       | 18       | 4.6   | 0.32  |
| PZT-24              | 1340          | 42                       | 38       | 10.2     | 2.6   | 0.34  |

4. Conclusion

The soldering technology for piezoelectric elements fastening using the reactive foil gave excellent results on the porosity of the seam. The application of the proposed technology allows to obtain seams void ratios not exceeding 2.5 % per element area, which is much better than in case of classical soldering. This fact benefits much for the use of piezoelectric elements in microwave devices, as an increase in the porosity of more than 5% in such devices may result in significant system deviations when tuning or operating the module. Classical soldering can lead to void ratios from 10 % to 60% depending on the soldering material and method, therefore, the elements’ applicability may be narrowed due to the chosen soldering method.

Moreover, the absence of the SHS-process influence on the resonant frequencies, internal electrical capacity the dielectric losses of the piezoelements has been proved by corresponding measurements.

All the studied samples were subjected to the strength and climatic tests, showing soldering characteristics no worse than those of the control samples joined using the standard POS-61 type solders.

To sum up, the proposed technology has several advantages:

- it does not require post-cleaning of the seam region with chemicals after the soldering;
- the reaction taking place inside the soldering layer does not damage the crystalline structure of the piezoceramic elements;
- the mentioned reaction does not produce critical negative effect on the electrical properties crucial for receiving and transducing systems.

At the same time, the question remains open about the possibility of improving the strength characteristics of the grown multilayer material.

References

[1] Sharapov V and Sotula Zh 2012 *Electronics: STB* **5(00119)** 96–102
[2] Sharapov V, Musienko M and Sharapova E 2006 *Piezoelectric sensors* (Moscow: Technosphere) 24-45
[3] Sharapov V 2010 *Piezoceramic sensors* (Springer Verlag) **9** 56-59
[4] Sharapov V, Vladisauskas, Bazilo K, Kunitskaya L and Sotula Zh 2009 *Methods of synthesis of piezoceramic transducers: spatial energy force structure of piezoelement* Ultrasound **4(64)** 44–50
[5] Embil I 2011 *Akustisten pietsokeraamisten elementtien ja elektrodien soveltaminen eri tavoin, Doctoral dissertation* Institution of Higher Education "St. Petersburg State Maritime Technical University" St. Petersburg 22-65
[6] Lihov A, Rudjak V, Pugachev S and Hohlov D 1993 Ferroelectric and piezoelectric 3(0024) 48-53
[7] Pugachev S 1997 Metallization of piezoceramics in a high-frequency electric field St. Petersburg 120-127
[8] Panich A 2009 Piezoelectric actuators (Rostov-on-Don) 28 – 117
[9] Kvashenkina O, Gabdullin P and Arkhipov A 2018 IEEE International Conference on Electrical Engineering and Photonics 8564437 202-206
[10] Bogdanova Y 2010 Adhesion and its role in securing the strength of polymer composites Tutorial 1 7-45