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On the Precision Preparation of Samples for Atom Probe Tomography Using a Focused Ion Beam in a SEM

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Abstract—Atom probe tomography is a modern and dynamically developing method of material investigation. It allows studies of the structure of matter at the atomic scale. The physical fundamentals of this method require a specific size, shape and conductivity type of the sample. To expand the analytical capabilities of atom probe tomography, a technique for preparing samples using a focused ion beam in a scanning electron microscope is studied and implemented in this work. The basic principles of this approach are demonstrated; its advantages, disadvantages and important practical aspects are described. To protect a fabricated sample from the influence of environment upon its transport to an atom probe tomograph, it is suggested a platinum coating be used. The atom-probe-tomography analysis of samples prepared with a focused ion beam is carried out. The effects of using such a sample preparation technique are studied.

Keywords: Atom probe tomography (APT), scanning electron microscope (SEM), focused ion beam, FIB, sample preparation

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1. INTRODUCTION

The development of modern analytical methods of ultramicroscopy provides an increase in detail of the structural-phase state of materials down to the atomic scale. Atom probe tomography (APT) can reconstruct 3D position and chemical nature of atoms in the analyzed volume of complex multicomponent materials with the help of evaporation by electric-field pulses or by laser and consequent recording of the evaporated atoms and computer analysis of the data [1].

This study deals with such a significant aspect of the atom-probe-tomography investigation as sample preparation, since the conditions of evaporation of atoms of the sample and their recording impose strict requirements on the size and shape of the sample. Since a specimen for APT investigation must have the form of a sharp-pointed needle with a radius of curvature of its tip equal to ~50 nm and a cone angle not exceeding 11°, the preparation of specimens of different materials is a technically challenging task. For most metals and their alloys, sample preparation is carried out by means of electrochemical etching, whereas, the preparation of samples of some other metals, semiconductors, dielectrics, and composite materials by means of the electrochemical method is complicated or impossible. In recent years, in order to solve this problem, systems combining a scanning electron microscope (SEM) with a focused ion beam (FIB) have been widely used all over the world. The dual-beam SEM-FIB systems includes also a gas-injection system (GIS) and a micromanipulator.

Common approaches to the preparation of APT samples of different materials with the help of SEM-FIB systems are presented in [2–4]. However, the peculiarities of different instruments and the necessity of solving fundamentally new problems require improvement in and development of this method. This work presents the results of development of the technique of APT-sample preparation in a Helios Nanolab 600 scanning electron-ion microscope and shows the potential capacities and some peculiarities of the used approach.

2. ATOM PROBE TOMOGRAPHY

The atom probe tomography combines the principles of field-ion microscopy and time-of-flight mass spectrometry. A high spatial resolution of APT is based on the projection principle of the field-ion microscope designed by E. Müller in the 1950s [5]. The applied potential difference between a pointed specimen and a detector provides the movement of ions along defined trajectories, which allows one to unambiguously establish the connection between the

input coordinates of an atom coming to the position-sensible detector and the output coordinates it had at the moment of leaving the sample. At the same time, the applied potential difference is always lower than the threshold of field evaporation of the ion from the specimen surface. It is always an additional pulse action that causes ion evaporation from the specimen surface [6] and it allows one to record the moment of time when the ion left the sample and to determine the flight time of the evaporated ion after having recorded the moment when it comes to the detector. As a result, the obtained data allow one to determine the mass-to-charge ratio of the particle evaporated from the specimen and its position at the sample.

Atom probe tomography makes it possible to carry out investigations of the nanoscale structural-phase features of materials revealing even aggregates of a few atoms and establishing the chemical nature of each of them. By analyzing the samples undergoing various thermal and radiation exposures with the help of the atom probe, it is possible to trace the kinetics of the growth or dissolution of nanoscale inclusions, the change in their composition and element distribution, the evolution of the nanostructure of the material in general etc.

For the first time, the operating prototype of a tomographic atom probe was presented in 1980. Later, different conceptions of APT instruments were suggested and tested. In Russia, the APT investigations started in 2003 in the laboratory of the atomic-scale research of condensed matters of the Institute of Theoretical and Experimental Physics at the energy-compensated optical tomographic atom probe "ECOTAP" CAMECA [7]. The electric-pulse evaporation of the sample atoms is used in this instrument, so, it allows to investigate only conducting materials. The typical obtained data volume is ~ $10 \times 10 \times 100$–500 nm^3 and the detection rate is ~ 1–10 atom/s.

A considerable part of the research carried out with the help of "ECOTAP" is devoted to investigations into the nanostructure of reactor materials both in the initial state [8, 9] and after exposure to radiation by neutrons or ions [10, 11]. In all mentioned cases, APT analysis made it possible to reveal the features of the chemical composition of the nanostructure of steels unavailable to other methods.

In recent years, the atom-probe-tomography method has actively developed, new types of detecting [12] and evaporating systems [13, 14] have designed, and algorithms of data reconstruction have improved [15]. With the purpose of developing this method, enhancing the characteristics, and enlarging the range of investigated materials, a prototype of an atom probe with laser evaporation APPLE-3D was designed and put into operation at the Institute of Theoretical and Experimental Physics [16, 17]. In the designed prototype, controlled evaporation is carried out with the help of a pulsed laser source. The application of the laser allows the investigation of a broad range of materials: metals, semiconductors, ceramics, glass and even some biological objects [18–20]. The use of a position-sensitive delay line detector (DLD) as a detecting system makes it possible to considerably increase the data collection, namely, by an order of magnitude in comparison with the standard detector "ECOTAP". The results of investigations carried out in APPLE-3D showed that the area of analysis is approximately $50 \times 50 \times 1000$ nm^3. The requirements to the sample do not differ from those for "ECOTAP". The sample should be a thin needle with a radius of curvature equal to 50–100 nm^3; the conicity of the sample should not exceed 11°. The other end of the sample is fixed in a special holder providing the appropriate electrical and thermal conductivity, since the study is carried out under conditions of high vacuum at a temperature of about 20 K and at a high voltage (10–20 kV).

3. EXPERIMENTAL

Sample Preparation for APT Analysis in a SEM-FIB

Modern dual beam system provide not only different ways of investigating a sample using specialized detectors, but also allow the preparation of samples in situ. To prepare APT-samples, one uses the possibilities of high-resolution scanning electron microscopy as well as ion milling, etching, evaporation and deposition of the substance and displacement by means of a micromanipulator. It should be also noted that the sample preparation for APT has a number of procedures similar to that for transmission electron microscopy. The main physical mechanism of material removal in a SEM-FIB is precise ion-beam sputtering atoms of the sample's surface.

A specimen for APT analysis is prepared from a bulk sample by means of mechanical- or chemical-treatment methods such as cutting, polishing, and etching. These methods are not always applicable to microscopic objects and hardly controllable. However, with the help of an ion beam, it is possible to perform cutting, polishing, and etching. In addition, SEM allows to visualize and control these processes by carrying out measuring at scales from millimeters to nanometers. By using various detecting systems in modern SEM and analyzing the electron image contrast, absorbed current, X-ray and Raman spectra, as well as by means of reflection high-energy electron diffraction and other methods, the required microscopic feature of the structure or composition of a macroscopic object can be visualized and localized. The required area can be located under the surface of the sample. In this case, ion etching to the given depth allows one to cut out such an area for subsequent analysis.

Dual beam microscope makes possible to prepare samples for APT analyses from nanoscale objects. For example, the application of a substance evaporation

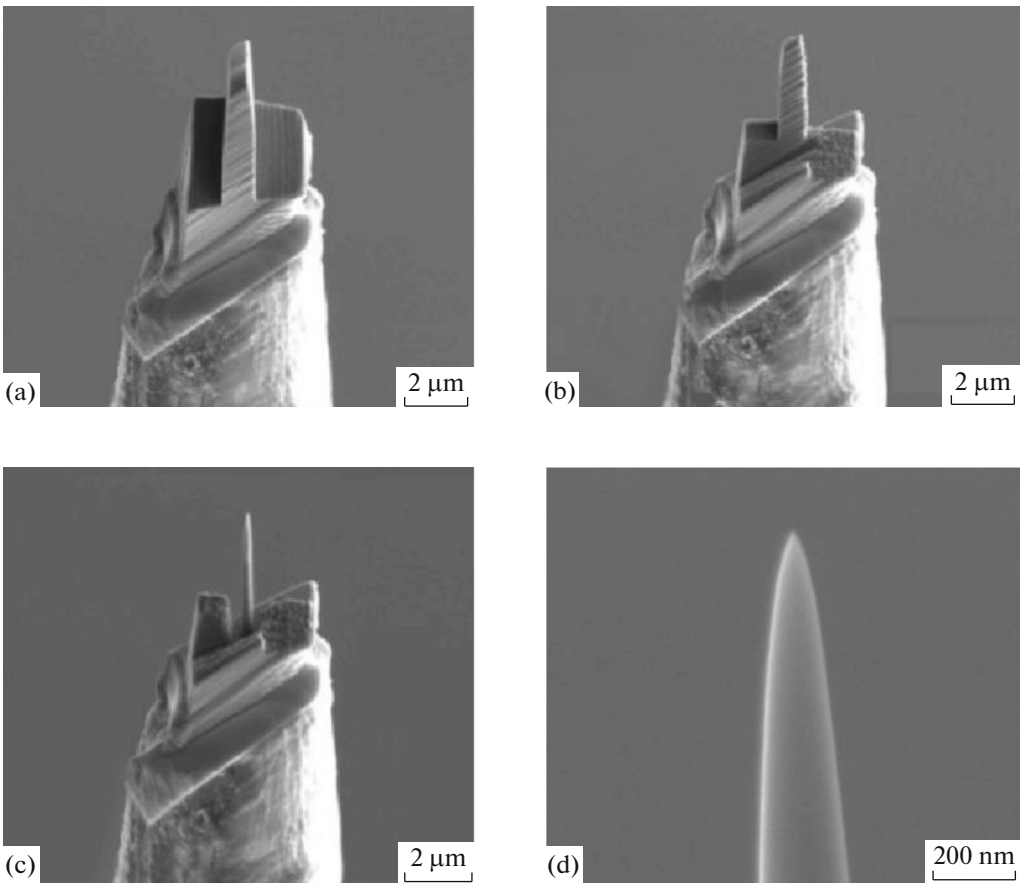

Fig. 1. Microphotograph of the process of step-by-step etching of a blank by an ion beam from various directions (a, b) and precision sharpening (c), and an enlarged image of the tip suitable for analysis in the APT (d). The images (a), (b), and (c) are borrowed from [24].

system enables the preparation of APT samples including objects whose sizes do not allow one to carry out direct manipulations with them, for instance, nanoparticles. Being covered by a layer of some substance, such particles can be studied as inclusions in the volume of a prepared sample [21]. There are also preparation methods for nanoscale wires for APT analysis [22].

The main procedure used in the SEM-FIB for the preparation of APT samples is the precision sharpening of bars which can be preliminarily thinned by an electrochemical method and have a diameter of the tip down to tens of μm. If the diameter of the bar's tip is above 2 μm, one should start with ion beam cutting of the bar. In this case, an ion beam with a high current (up to tens of nA), directed perpendicularly or at an angle to the needle bar, sharpens it from two or more directions (Figs. 1a, 1b). When the sizes of the needle are appropriate to start precision processing (the diameter of the sharp point does not exceed 1 μm), one places the needle coaxially to the ion beam and sharpens it with an ion beam with a small current (10–50 pA) with the use of a circular mask, subsequently reducing the current and size of the mask (Fig. 2). The diameter of the central zone of the mask, under which the tip of the sample is formed, must be equal to about 200 nm in the case of good focusing of the ion beam whose characteristic effective diameter at a given current does not exceed 20–50 nm. As a result of such a preparation procedure, a sample with the required shape and size, suitable for APT analysis (Figs. 1c, 1d), is obtained.

A method appropriate for all materials is the lift-out method consisting in cutting-out the bar from the sample surface and welding it to a base of conical or pyramidal shape with a truncate (or rounded) apex, one end of which is suitable for special sample holder. The base with a thickness of the tip of about 1–2 μm can be made of metal by means of electrochemical etching. The base tip must be preliminarily truncated perpendicularly to the axis of the base by an ion beam in order to form an area with a width of about 2.5 μm. In the ideal case, the bulk sample must have a flat surface from which a bar will be cut. The bulk sample and one or more bases are placed into the chamber in such a way that in the initial state of the sample stage, the sample's plane is perpendicular to the electron-beam axis, while the axes of the bases are parallel to it. A

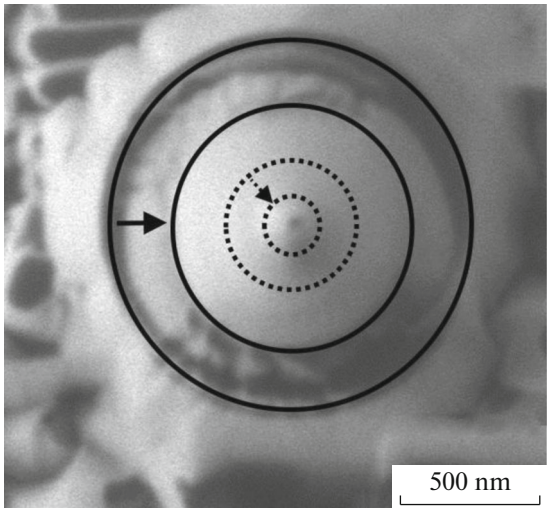

Fig. 2. Circular masks of different sizes on the microphotograph of a sample. The boundaries of ion etching: the external boundary is shown by a solid line, the internal, by a dotted line. The arrows indicae a reduction in the etching area upon transition to the finishing stage of sharpening.

deviation of a few degrees is acceptable and can be adjusted by an operator for electron or ion images. If additional treatment of the surface by the ion beam is not required, a selected large flat area of the blank with a width of 2–4 μm is coated with a protective layer of platinum, tungsten, or carbon with a thickness of up to 500 μm depending on the task description. After that, at the edges of the area, one etches hollows at an oblique angle until a bridge of rectangle shape is formed. One of the fixing points of the bridge is etched (Fig. 3a). The needle of the micromanipulator is brought up to the free end of the obtained bar and fixed by means of metal evaporation (as a rule, one uses for this purpose platinum or tungsten). Then, the second fixing point of this bar is cut and it remains suspended on the needle of the micromanipulator (Fig. 3b). The needle of the manipulator with the bar is brought to the base of conical shape with a truncated apex, contacts with it and fixed by GIS (Fig. 3c). The required area with a width of a few μm is cut from the sample fragment and remains fixed to the base (Fig. 3d). The residual of the fragment fixed to the manipulator can be used to prepare a few replicas of the sample, provided that there are a few bases. When the entire fragment is used or the manipulator is drawn out of the operating area, we can start to perform additional mounting of bars on the bases and precision sharpening of the obtained tips. To provide secure and symmetrical mounting of a fragment on the base, it might be necessary to perform step-by-step rotation of the base by a certain angle with metal evaporation after each turn. The sharpening of the bars-on-tips is similar to the above-described technique of sharpening.

It should be noted that any deviation of the ion beam from the given geometry of radiation or its defocusing at the finishing stage of precision sample sharpening may lead to negative consequences: from bending of the sample to its complete failure. It is the time instability of the ion-optic system (but not beam focusing) that is a parameter which limits the minimum size and conicity of the prepared sample. Thus, when continuing to sharpen a sample whose radius of tip curvature is already equal to about 50 nm, the probability of damaging the sample increases several times.

Peculiarities of Storage and Transportation of the Samples for APT Analyses

The performed series of work demonstrated that the prepared samples quickly become unsuitable upon their transportation from the dual beam microscope to the APT because of vibrations and/or prolonged exposure to air. It is evident that the samples obtained by means of ion etching are chemically and physically unstable objects and are easily deformable and easily oxidized. The process of welding the sample to the base can be controlled only visually; in the process of precision sharpening, the welding spot is exposed to the ion beam, so, the strength of the joint may be weakened, which can lead to sample failure under exposure, temperature, vibrations or due to the effect of all of these factors in combination. The mechanisms of failure, deformation, and oxidation are at present poorly understood. In the case of prolonged transportation, it is suggested to use a vacuum vibration-resistant transport container. It should be noted that depending on the experience of the operator, equipment reliability, and its parameters, the losses due to storage and transportation of the samples can be between 10 and 50% and are considerably reduced in the case of direct proximity of the dual beam microscope and the APT. It is of particular importance, since sample preparation by the lift-out method takes about two hours per sample provided the multiple use of one fragment lifted-out from the sample surface. The finishing sample sharpening takes about an hour per sample depending on the initial size of the blank.

Even in the case of direct proximity of the instruments, one cannot avoid losses caused by surface oxidation of the prepared samples. To protect the prepared samples from exposure to air, in this work we tried coating the prepared samples with a protective layer of platinum with the help of an evaporating system and an electron beam. The samples coated in such a way underwent oxidation to a lesser degree; however, when analyzing the samples in the APT, platinum was found over almost the entire investigated volume, which is evidence of the penetration (diffusion) of the coating atoms (in our case platinum) into the sample material. It should be noted that the interpretation and correction of the data of APT analysis of such samples is possible with the use of reference samples without a

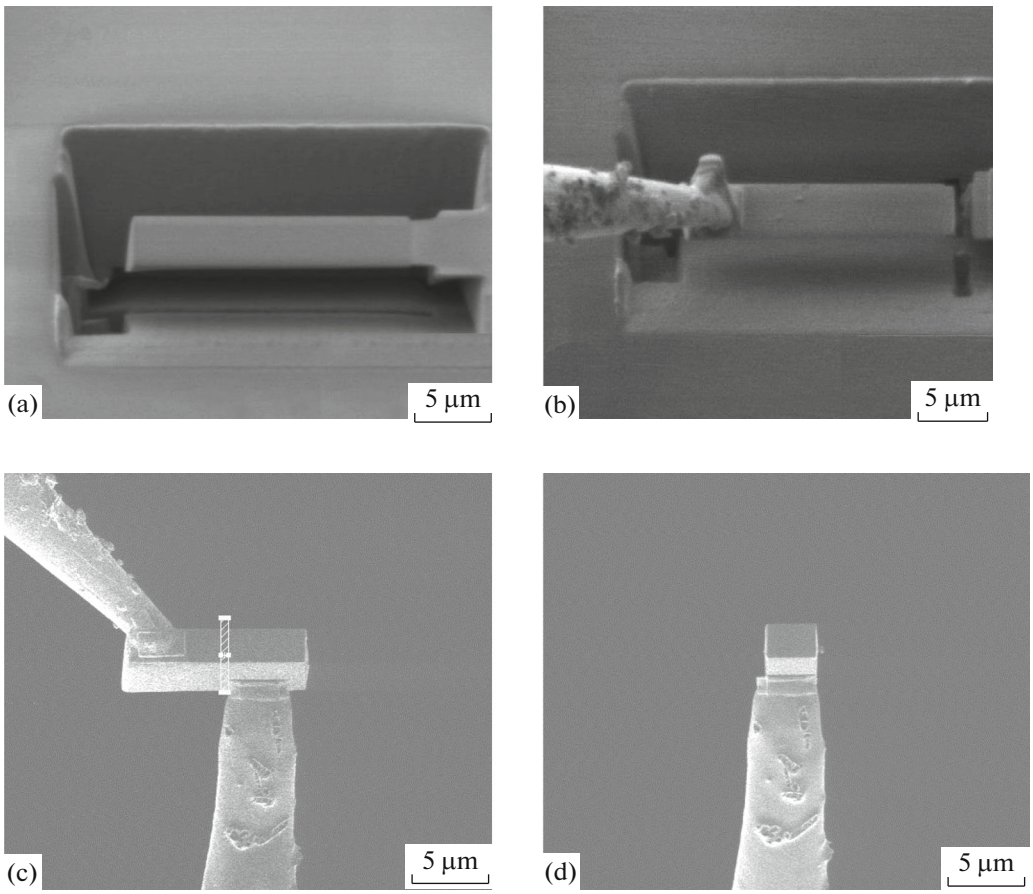

Fig. 3. Principal stages of sample preparation by the method of cutting from the sample surface (lift-out method). The result of preparation of a bar fixed at one point (a). Fixing a manipulator to this bar (b). Mounting the bar to the base (c). The base with a fixed sample (d).

coating, but the description and development of such methods go beyond the framework of this work. In some cases, it is possible to reduce the penetration of coating atoms into the sample.

The performed studies show that coating the samples with platinum results in an increase in their size, which affects the results of APT analyses. Fig. 4 shows microphotographs of the prepared sample without a coating (Fig. 4a) and with a platinum coating (Fig. 4b). One can observe a considerable thickening of the sample after coating. Therefore, after coating with a protective layer, it is reasonable to perform additional precision sharpening of the sample. Improvement in the suggested method of coating samples made of various materials and the development of variants of tungsten or carbon coating can significantly improve the "survivability" of samples and reduce the effect of coating on the results of APT analysis.

4. RESULTS OF APT ANALYSES

Refinement of the complete cycle of research from sample preparation in a SEM-FIB to its investigations with the help of APT was carried out for steels and alloys, the major part of which had already been investigated with the use of the standard sample preparation technique in which the samples are sharpened by the electrochemical method. In this case, a focused ion beam was used for the precision finish sharpening of the metal samples. The results of the performed investigations are comparable to the results shown by the samples prepared by the traditional electrochemical method; however, atoms of gallium are found virtually over the entire volume of the sample with their concentration increasing at the surface layer. It proves the necessity of control and minimization of the ion-beam effect on the sample at the stage of finish sharpening. It is known that the penetration depth of gallium ions into condensed matter varies from several nanometers to tens of nanometers depending on the ion energy and the angle of incidence; therefore, the effect of ions on a sample in the direction perpendicular to its surface must be minimal. It should be noted that despite the fact that APT analysis shows the presence of gallium atoms in the investigated region, it does not have a significant effect on the results of analysis over all the

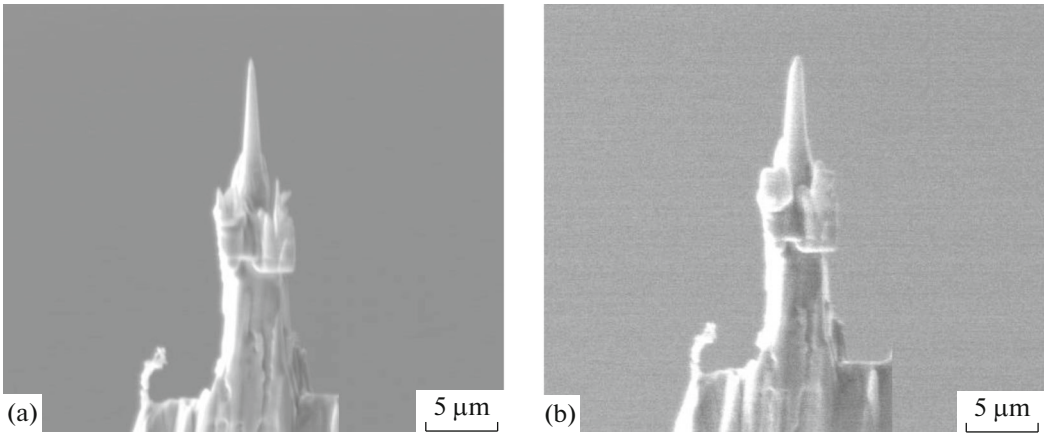

Fig. 4. Microphotograph of the sample prepared for APT analysis (a) and the same sample after having coated it with a platinum layer (b).

components of the material under study. Taking into account the results of [4, 23], we used the minimum possible currents of the ion beam when preparing the samples.

To illustrate the results of APT analysis, Fig. 5 presents maps of the spatial distribution of elements in a sample of Ti–20Zr–1.7Mo alloy, which were obtained on a APPLE-3D. At the finishing stage of preparation, the sample was coated with platinum. A volume of $10 \times 10 \times 100$ nm^3 was considered. As one can see, platinum from the evaporated protective layer penetrated into the depth of the given volume and is distributed non-uniformly, despite the fact that evaporation was caused only by the electron beam. The distribution of gallium in the considered volume has a non-uniform character and indicates that the considered region was in proximity to the sample surface.

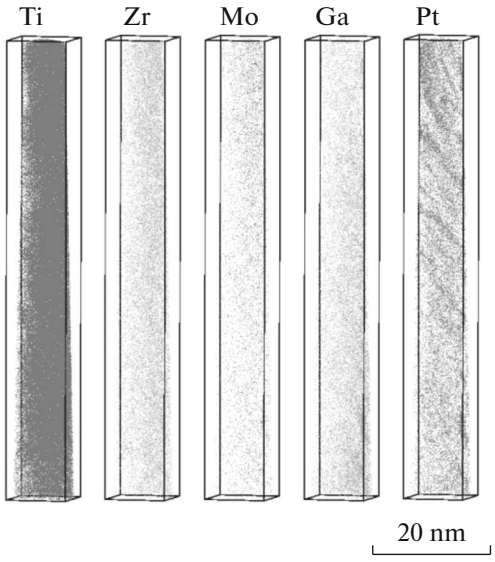

Fig. 5. 3D maps of the spatial distribution of chemical elements in the considered volume $10 \times 10 \times 100$ nm^3. Each point represents a single recorded atom.

CONCLUSIONS

In the work, the method of sample preparation for atom probe tomography with the help of SEM-FIB was studied and tested. We considered in detail some features of this method which can be the consequence of the specific features of the used instrument and the influence of its parameters, as well as the physics of the interaction between the ion beam and the substance and the diffusion of elements of the protective layer. An important element of the entire procedure of the study is the transportation and storage of the prepared samples. To protect the samples from negative environmental effects, the method of sample coating with platinum is suggested. For sample transportation at long distances, it is proposed to use a vacuum vibration-resistant transport container. In the work, the samples of titanium alloy and some other materials were prepared and studied, the results of APT analysis revealed the penetration of beam ions into the surface layer of the sample material, as well as the diffusion of platinum atoms from the protective layer to the volume investigated in the APT. At the same time, these processes do not have a considerable effect on the results of APT analyses of the material itself. It is proved that the factor influencing the quality of the finish sharpening of samples is the instability of the ion-optical system of the used microscope.

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