

Condensed Matter and Interphases

Kondensirovannye Sredy i Mezhfaznye Granitsy
<https://journals.vsu.ru/kcmf/>

Original articles

Research article

<https://doi.org/10.17308/kcmf.2021.23/3672>

Anodic behaviour of manganese germanide Mn_5Ge_3 in a sodium sulphate aqueous solution

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Abstract

Germanides are an interesting class of two-component systems which consist of metal and germanium. They are similar in their structure with silicides but have the specific properties. The target of the investigation was finding the main anodic electrochemical behaviour mechanisms for magnesium germanide Mn_5Ge_3 in an Na_2SO_4 aqueous solution.

Electrochemical behaviour of manganese germanide obtained by Czochralski method was investigated by polarization curves and electrochemical impedance spectroscopy methods and accomplished by microscopy data. Individual manganese and germanium were investigated in the same way for comparison. It was established that in the anodic oxidation process germanium is the potential-determining component. The passivation process associated with the formation of surface oxide films was accomplished by the current density oscillations appearing due to the bad adhesion of oxide film to the surface of the sample, its imperfection and discontinuity. The nature of oxide film formed in the polarization process was partially established. The dependence of the anodic behaviour of the sample on the sulphate concentration was established: in the diluted solutions the passivation occurs at more positive potentials than in the concentrated. This phenomenon can be explained by the different mechanisms of anodic oxidation in the solutions of different concentrations.

Keywords: Manganese, Germanium, Manganese germanide, Oxide films, Anodic oxidation, Impedance spectroscopy

Acknowledgments: the research was supported by Perm Scientific and Educational Center “Rational use of mineral resources”, 2021.

For citation: Rakityanskaya I. L., Myasnikov D. A., Shein A. B. Anodic behaviour of manganese germanide Mn_5Ge_3 in sodium sulphate aqueous solution. *Kondensirovannye sredy i mezhfaznye granitsy = Condensed Matter and Interphases*. 2021;23(4): 535–542. <https://doi.org/10.17308/kcmf.2021.23/3672>

Для цитирования: Ракитянская И. Л., Мясников Д. А., Шейн А. Б., Исследование анодного поведения германида марганца Mn_5Ge_3 в водном растворе сульфата натрия. *Конденсированные среды и межфазные границы*. 2021;23(4): 535–542. <https://doi.org/10.17308/kcmf.2021.23/3672>

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1. Introduction

In the modern world, much attention is paid to the search for new materials with high corrosion resistance over a wide range of aggressive media. Such materials are transition metal silicides [1, 2]. However, the study of germanides of the same metals, which are close to silicides in structure [3] but do not have a high resistance to corrosion, may also be interesting mainly due to the elucidation of the mechanism of dissolution of systems consisting of several components, differ by their physical and chemical properties.

Manganese is a rather active element; therefore, its metal-like compounds, including silicides and germanides, have properties different from similar systems of the iron triad, studied in detail earlier [4]. There is an array of data obtained as a result of the study of electrochemical processes occurring on the silicide Mn_5Si_3 and manganese monosilicide $MnSi$ in acidic electrolytes [5–7]. The same two-component systems in alkaline media are less studied [8, 9]. Now, data on the behaviour of manganese silicides and germanides in aqueous solutions with a pH close to 7 are limited, although majority of the electrolytes in various industries are neutral media. The publications mainly contain data on the electrochemical and corrosive behaviour of metal silicides of various compositions [10–14], while such studies for germanides are less common [15, 16].

2. Experimental

The object of the study was a double metal-like system – manganese germanide Mn_5Ge_3 obtained by the Czochralski method [1]. The germanide sample is soldered to the copper wire with a silver-containing conductive glue. The entire electrode was insulated with epoxy glue, excluding the working surface. The electroactive surface area was 0.15 cm^2 .

The preparation of the electrode surface before the experiment was carried out as follows: the electrode was mechanically cleaned and polished with emery paper, successively changing its grade from 1000 to 2500. The prepared surface was degreased with 96% ethyl alcohol and rinsed with distilled and deionized water. A saturated silver chloride electrode was used as a reference electrode. The counter electrode was platinum.

Deionized water ($R = 18.2\text{ M}\Omega$), obtained in a Milli-Q Advantage A10 water distiller (Germany), and dry sodium sulphate powder (chemically pure grade) were used for the preparation of electrolyte solutions. The studies were carried out in a standard YSE-2 electrochemical cell. Polarization and impedance measurements were performed using a Metrohm Autolab PGSTAT302N potentiostat/galvanostat. The polarisation curves were recorded in the potentiodynamic mode at the scan rate of 1 mV/s and a temperature of $20 \pm 5\text{ }^\circ\text{C}$.

The range of frequencies used in impedance measurements $f(\omega/2\pi)$ were from 100000 Hz to 0.05 Hz , the amplitude of the alternating signal was 10 mV . Before measuring the impedance, the electrode was kept in a solution at an appropriate potential until stable current density values were achieved. The impedance data were processed using NOVA 2.1.4 program.

The studies were carried out under natural aeration and stationary diffusion conditions. The cell was washed several times with tap, distilled, and deionized water before work. In the case of strong contamination of the cell with corrosive products, it was washed with a hot chrome mixture.

Microscopic measurements were carried out using an HITACHI S-3400N Scanning Electron Microscope with a BRUKER attachment for X-ray microanalysis.

3. Results and discussion

3.1. Polarisation measurements

When studying the electrochemical behaviour of multicomponent systems, it seems appropriate also obtain information on the analogous behaviour of simple substances which are constituents of such systems under similar conditions. A comparative study of the anodic behaviour of manganese, germanium, and manganese germanide in a $0.5\text{ M Na}_2\text{SO}_4$ solution was carried out by the polarisation curve method (Fig. 1).

The dissolution of germanium in sodium sulphate occurs uniformly, without noticeable peaks in the anodic curve. With an increase in the anodic polarisation, the currents increase, but the rate of increase is not the same in different areas, which indicates a change in the dissolution mechanism and, possibly, a change

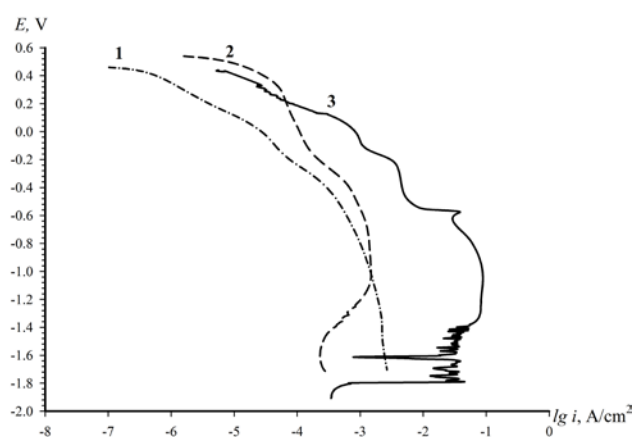


Fig. 1. Polarization curves for manganese germanide Mn_5Ge_3 and its individual components in 0.5 M Na_2SO_4 solution: 1 – Ge; 2 – Mn; 3 – Mn_5Ge_3

in the composition of corrosion products. This is in good agreement with the literature data [4, 17], where it is stated that anodic dissolution of germanium in aqueous solutions of different compositions can form a mixture of hydrated oxides GeO and GeO_2 as well as metagermanic acid H_2GeO_3 , which slow down the dissolution rate only in the case of accumulation of a sufficiently thick layer of phase oxide.

Manganese is an active metal, which forms many oxidized forms upon anodic polarization in aqueous media [18]. The curve of its anodic dissolution is in good agreement with the data of the Pourbaix diagram, according to which, starting from a potential of 0.1 V, Mn_3O_4 and Mn_2O_3 oxides are sequentially formed on the metal surface, and finally, MnO_2 is formed at a potential of 0.8 V, the accumulation of which slows down the rate of dissolution of the metal. In a 0.5 M sodium sulphate solution, the dissolution rates of pure germanium and manganese are comparable.

Upon anodic polarization manganese germanide Mn_5Ge_3 demonstrates a high corrosion rate, which is 1–2 orders of magnitude higher than for its constituent pure components. Corrosion potentials for germanium and manganese were $E_{cor} = -0.46V$ and $E_{cor} = -0.56 V$, respectively; for manganese germanide, $E_{cor} = -0.47 V$, which suggests that germanium is the potential determining component. The characteristic potentials of the anodic curve for manganese germanide, at which the Tafel slope changes, mainly coincide with the analogous potentials

for germanium polarisation curve. The latter suggests that in this situation, the features of the anodic processes on the sample are mainly due to its non-metallic component. However, with deep anodic polarisation, peaks appear at potentials +0.6 V (peak I) and +1.25 V (peak II) on Mn_5Ge_3 curve, which are not typical for both Mn and Ge. Moreover, at a potential of +1.4 V, a rather long region of current density oscillations begins, behind which a decrease in the current density was recorded, and, therefore, the dissolution processes slowed down.

The concentration of sodium sulphate affects the processes occurring during the anodic dissolution of the sample (Fig. 2). With concentrations above 0.5 M, only the dependence of the dissolution rate on the concentration is observed, the potential of all peaks of active dissolution remains constant, only its current decreases. With a decrease in the concentration of sodium sulphate to 0.25 M and below, the potentials of both peaks of active dissolution shift to the region of more positive values, which may be associated with a slowdown in the dissolution process due to a decrease in the electroconductivity of the solution. In addition, sulphates, not participating directly in the surface transformation process, can be its activators, and, thus, a decrease in their concentration can lead to diffusion limitations.

The region of anodic current density oscillations is also subjected to the influence of the electrolyte concentration: with an increase in

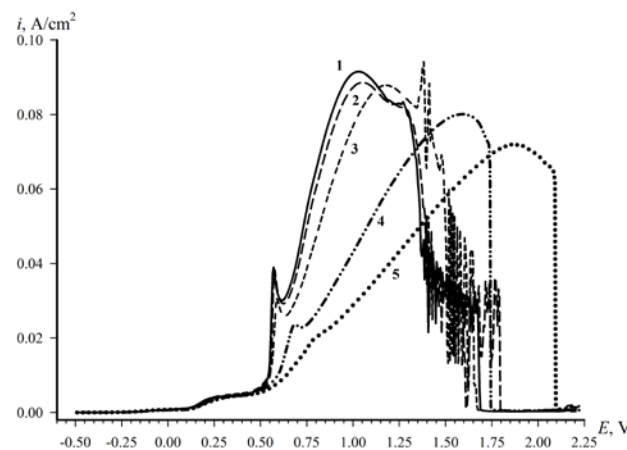


Fig. 2. Anodic polarisation curves for manganese germanide Mn_5Ge_3 obtained in Na_2SO_4 solutions of different concentrations: 1 – 1 M; 2 – 0.5 M; 3 – 0.25 M; 4 – 0.1 M; 5 – 0.05 M

the content of sulphate ions, it is observed at less and less positive potentials, and its range expands.

3.2. Impedance measurements

Nyquist plots at the corresponding potentials in a solution of 0.5 M sodium sulphate are shown in Fig. 3. As the potential shifts towards more positive values, the graph takes on the form of two clearly separated semicircles and an inductive arc.

In the potential range from -0.1 V to 0.8 V, the impedance of the system decreased, then slightly increased in the active-passive transition area. The complex nature of the curve reflects the multi-stage nature of the polarisation process: such graphs are typical for electrodes characterised by the variety of adsorbed corrosion products [19]. This confirms the earlier assumptions about the

formation of an oxide layer on the sample surface. In all spectra, the HF semicircle corresponds to the processes occurring on the hydrated oxide film and the interface between it and the electrolyte, while the LF semicircle characterizes the interface between the oxide film and the electrode surface.

The appearance of an HF pseudo-arc can be associated with several factors, first of all, with the phenomenon of capacitance dispersion, occurring due to the peculiarities of the measuring system. Often, such phenomena occur due to deficiencies in the reference electrode and the design of the cell. In this case, such part of the spectrum is an artefact; therefore, it was not taken into account when analysing the spectra [20, 21].

On all impedance spectra between two semicircles there is an inductive loop gradually

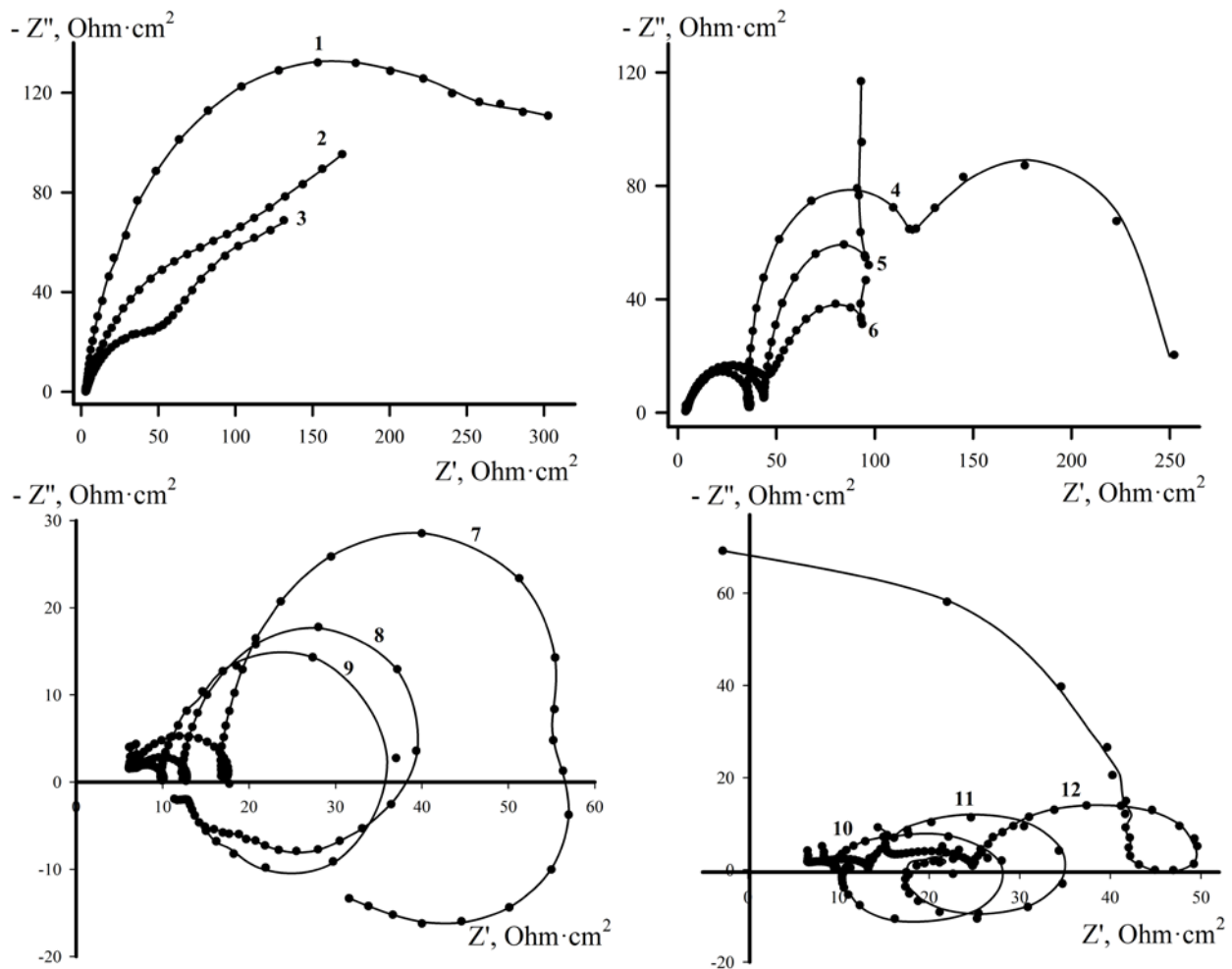


Fig. 3. Nyquist Plots for manganese germanide Mn_5Ge_3 in 0.5M Na_2SO_4 solution at the following potentials: 1 – -0.1 V; 2 – 0 V; 3 – $+0.1$ V; 4 – $+0.2$ V; 5 – $+0.3$ V; 6 – $+0.4$ V; 7 – $+0.5$ V; 8 – $+0.6$ V; 9 – $+0.7$ V; 10 – $+0.8$ V; 11 – $+0.9$ V; 12 – $+1$ V

shifting to the right, which according to [22] is associated with an increase in surface roughness and stabilization of the oxide layer containing adsorbed anions. The surface roughness was presumably increased due to the formation of micropores due to the accelerated diffusion of SO_4^{2-} particles in the oxide layer.

The straight line on the Nyquist plot was obtained using the Voith scheme. All spectra are characterized by two positive time constants, which can be assessed for reliability using the Kramers–Kronig relations. The inductive component of the spectrum is characterized by a negative time constant; therefore, this part of the spectrum cannot be assessed for reliability using the Kramers-Kronig relations. As the amplitude of the alternating signal changed to 5 and 3 mV, the graphs of the impedance spectra did not change.

Due to the multistage nature of the process, the impedance spectra were analysed by the characteristic frequencies f determined based on

the points of inflexion on the complex plane. The dependence of the characteristic frequencies on the applied anode potential is shown in Fig. 4.

Frequency f_1 , corresponding to the first semicircle and characterizing the process of charge transfer in the electrode - oxide film system, increased with increasing potential many times faster than the frequencies f_2 and f_3 , which correspond to the second semicircle and the inductance loop, respectively. In turn, the frequencies f_2 and f_3 also increased with increase in potential up to 0.8 V, at which the active-passive transition area begins. The increase of these characteristics is associated with the accumulation of a thick layer of poorly soluble surface compounds, which limit the process of removing the reaction products from the electrode. With a further shift of the potential to the anodic region, these frequencies decrease due to the fact that the layer of the formed intermediates begins to crack.

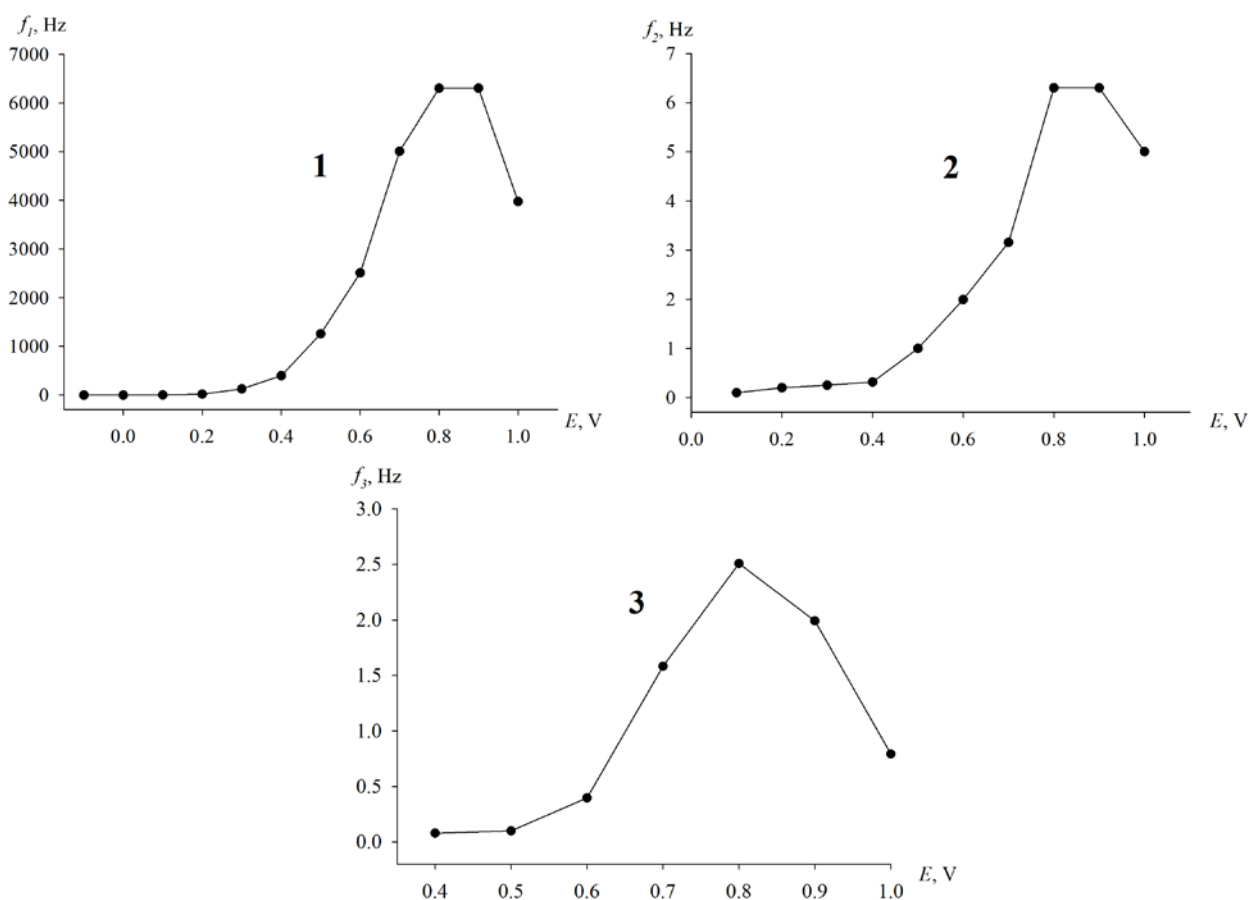


Fig. 4. Characteristic frequencies for Mn_5Ge_3 -electrode in 0.5 M Na_2SO_4 solution at different anodic potentials. 1) - HF (high frequencies) semicircle, 2) LF (low frequencies) semicircle, 3) LF (low frequencies) inductivity

The first time constant characterizing the HF semicircle changes most noticeably with increasing potential. The diameters of the HF and LF semicircles decrease with increasing potential, which indicates an increase in the intensity of the oxidation process. Products of $i \cdot R$ are shown in Fig. 5.

For the HF semicircle the $i \cdot R$ product increases monotonically, starting from $E = 0.4$ V. For the LF semicircle the $i \cdot R$ product also increases, but more smoothly than for the high-frequency semicircle. This means that the process of accumulation of the surface film somewhat reduced the possible rate of oxidation.

3.3. Microscopic examination of the structure

For the assessment of the composition and structure of the surface layer after polarization, micrographs of the surface were obtained and X-ray microanalysis was performed. When the electrode was kept in potentiostatic mode for ten minutes, an oxide layer was formed on its surface, which later started to exfoliate, which was especially noticeable when the electrode was removed from the electrolyte solution.

The micrograph obtained upon the potentiostatic incubation of the electrode in the region of the anodic peak at $E = 0.6$ V (Fig. 6) allowed the visualization of the morphology of the formed layer: areas free from oxidation products and areas with an exfoliating film were revealed on the electrode. X-ray spectral microanalysis of the film showed that it consists

of germanium and oxygen in an atomic ratio of 1:1. The fact that the hydrated form of oxidation products in air transforms into more stable oxide forms should be taken into account. In this regard, X-ray microanalysis showed the presence of only germanium oxide and the complete absence of manganese in the composition of the film.

On the micrograph obtained upon polarization up to $E = 1.8$ V (Fig. 7), a thick oxide film is clearly visible. According to X-ray microanalysis data, it also consists only of germanium oxide, but has denser structure. Manganese oxides can be formed at high positive potentials, but they were not revealed by this method of analysis.

4. Conclusions

Manganese germanide is rather unstable to anodic oxidation in a sodium sulphate solution. The mechanism of anodic dissolution includes several stages with the adsorption of intermediates. It is most probable that in a neutral environment, a high rate of Mn_5Ge_3 oxidation is associated with the uniform dissolution of both components, but only up to a potential of -0.45 V. With a deeper anodic polarization, the surface layer is depleted of manganese due to its selective dissolution from beneath the simultaneously formed germanium oxides layer. Thus, the passivation of manganese germanide at high potentials occurs due to the non-metallic component of the sample, while the reaction is controlled by the diffusion of manganese, which

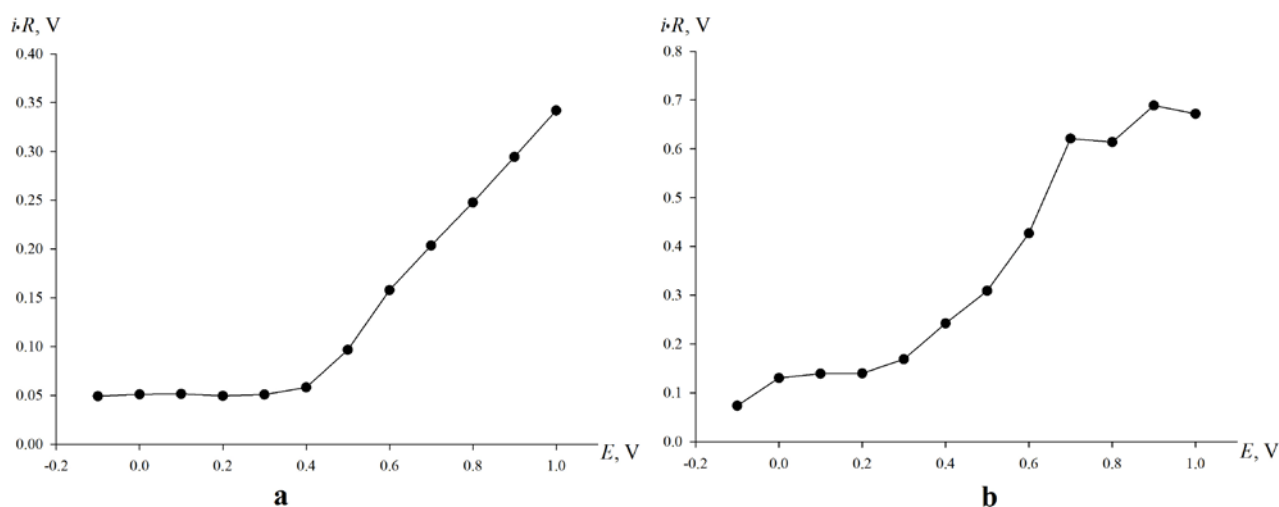


Fig. 5. Dependence of $i \cdot R$ on the potential of Mn_5Ge_3 -electrode in a 0.5 M Na_2SO_4 solution: a – HF (high frequencies) semicircle, b – LF (low frequencies) semicircle

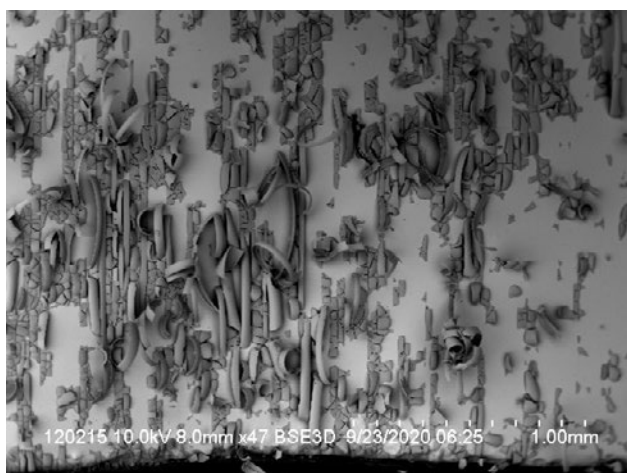


Fig. 6. Micrograph of Mn_5Ge_3 surface after 10 minutes anodic polarization at $E = + 0.6V$ in a 0.5 M Na_2SO_4 solution

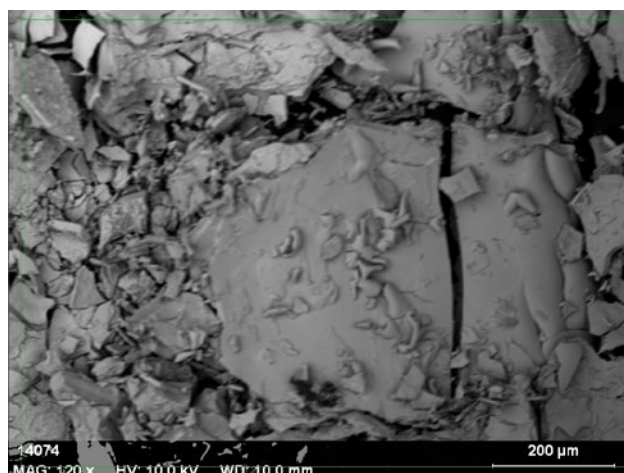


Fig. 7. Micrograph of Mn_5Ge_3 surface after 10 minutes of anodic polarization at $E = + 1.8V$ in 0.5 M Na_2SO_4 solution

is selectively ionized through the oxidation products of germanium.

Authors contributions

Rakityanskaya I. L. – the concept of research, the choice of research methods, writing the text, the final conclusions. D. A. Myasnikov – conducting research, review and text writing. Shein A. B. – general scientific guidance, final conclusions.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Received April 6, 2021; approved after reviewing April 30, 2021; accepted for publication September 15, 2021; published online December 25, 2021.

Translated by Valentina Mittova
Edited and proofread by Simon Cox