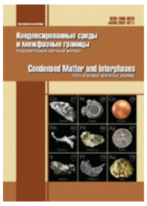

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Formation of oxide films on manganese silicide-germanides of various compositions during anodic polarization in an aqueous sodium sulfate solution

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Abstract

Objectives: Manganese silicide-germanides, with the general formula composition $Mn_5(Si,Ge)_3$, different in the quantitative ratio of silicon and germanium with the formula $Mn_5Si_{2.40}Ge_{0.60}$, $Mn_5Si_{0.60}Ge_{2.40}$, and $Mn_5Si_{0.15}Ge_{2.85}$, were subjected to anodic polarization in an aqueous sodium sulfate solution. The main objective of the study was the determination of the products of their anodic transformation in a non-oxidizing neutral medium and the identification of regularities of the formation of oxide films on their surface.

Experimental: The cyclic voltammetry method showed that the anodic oxidation process is not reversible. Polarization measurements were accompanied by subsequent monitoring of changes in the surface state using electron microscopy. The micro-X-ray spectral analysis was used for the determination of the ratio of elements on the surface before polarization of the sample and in the corrosion products.

Conclusions: The results of the study demonstrated that during the anodic transformation process for all materials, the fraction of manganese in the samples decreased, the fraction of germanium increased, and the fraction of silicon changed insignificantly. It was concluded that the dissolution of the material components occurs selectively: manganese was predominantly ionized from the solid phase of manganese germanide into the solution, and its content on the surface was reduced to insignificant amounts. Silicon and germanium formed loose oxide layers without good adhesion to a hard, manganese-depleted surface and did not provide a serious protective effect. Germanium (II) oxide and partially hydrated germanium (IV) oxide GeO_2 x H_2O were the main products of anodic oxidation that remained on the surface. Silicon oxide was also present in anodic oxidation products, but in lower quantities, and was not sufficient for the provision of the protective effect of the material.

Keywords: Silicide-germanide, Manganese, Germanium, Oxide films, Anodic oxidation, Sodium sulfate

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1. Introduction

The rapid development of modern technologies inevitably dictates the need to create and investigate the properties of new materials, which often represent a complex composition of components with significantly different properties. At the same time, modeling the electrochemical behavior of multicomponent and multiphase systems is a complex and non-trivial task, requiring a comprehensive approach and a wide range of methods. These methods should allow us to evaluate not only the final change in the material surface under the influence of an aggressive medium but also provide information about the kinetics of cathodic and anodic processes. The combination of cyclic voltammetry (allowing to assess the rate and reversibility of electrode processes) with electron microscopy and micro-X-ray spectral analysis (enabling to visually evaluate changes in the structure, qualitative and quantitative composition of the surface of the material) allows examining the various aspects of dissolution process of the material and to form a comprehensive view of the changes occurring on its surface. Manganese silicide-germanides, which have different ratios of silicon and germanium are suitable objects for such studies, since their individual components, manganese, silicon and germanium, have significantly different electrochemical behavior [1].

It is known that all individual components of manganese silicide-germanides are capable for oxidation in both acidic and alkaline media, forming products with various thermodynamic stability on the surface of the sample. Thus, during the oxidation of manganese, compounds in various oxidation states can be formed, none of which is capable to form the strong film with protective properties: in an acidic medium, soluble salts of divalent manganese are formed, and in an alkaline medium, manganese is in a passive state due to the formation of $Mn(OH)_2$ and at higher potentials, MnO_2 on the surface [2–5]. Silicon, due to the formation of poorly soluble SiO_2, protects the surface well from dissolution in acidic media, while in alkaline media its protective properties are not so significant [2, 6–8]. Germanium, despite its structure and some chemical properties like silicon, cannot form protective surface compounds in any of the previously studied media [2, 10].

Manganese silicide-germanides are two-phase structures consisting of silicide, silicide-germanide, and manganese germanide phases, with the amount of one or the other phase varying depending on the silicon or germanium content of the material [11].

It is known that Mn_5Si_3 and Mn_5Ge_3 “limiting” phases with respect to silicide-germanides during anodization form layers of oxidation products, which, in the case of manganese silicide, protect the surface of the sample from further destruction [9, 12]. In the case of manganese germanide, a defective layer of anodic transformation products, unable to protect the sample is formed [10, 12]. To date, there is no systematic data on the qualitative and quantitative composition of the products of anodic oxidation of manganese silicide-germanides with different ratios of germanium and silicon in neutral media. Nevertheless, data on the influence of the ratio of elemental silicon and germanium, as well as the phases formed in the material, on the formation of surface compounds can be used both for modeling the behavior of such three-component metal + two-non-metal systems and for practical use in the creation of semiconductor structures.

This work aims to compare the anodic behavior of manganese silicide-germanides with different ratios of silicon and germanium in the sample and to analyze changes in the surface microstructure of the materials and the products of their anodic oxidation.

2. Experimental

Manganese silicide-germanides with the following compositions: $Mn_5Si_{3-2.85}Ge_{2.85}$, $Mn_5Si_{3-2.40}Ge_{2.40}$, and $Mn_5Si_{3-0.60}Ge_{0.60}$, obtained according to the method described in [13], were subjected to multiple cyclic anodic polarization from the open circuit potential to the potential of thermodynamically possible oxygen evolution, followed by a return to the original potential. The surface of the sample was then examined microscopically using micro-X-ray spectral analysis. The methods of sample preparation and their study are described in detail in the study [13, 15]. The phase composition of the samples was confirmed by X-ray structural analysis [11].

With an increase in the fraction of germanium atoms in the sample, the phase composition of the material changes from a predominant content of the manganese silicide phase Mn_5Si_3 to the predominant content of the manganese germanide phase, Mn_5Ge_3.

3. Results and discussion

3.1. Polarization measurements and data from microscopic and micro-X-ray spectral studies of manganese silicide-germanides

Anodic CVA curves for $Mn_5Si_{3-0.60}Ge_{0.60}$ are shown in Fig. 1. From E = +0.2 V, the current density started to increase noticeably, which indicates active dissolution of the material. However, it was impossible to isolate a separate maximum on the curve; the peaks were not separated, and the oxidation processes of the components occurred at close potentials. At a potential of +1.6 V, a state of passivity occurred, and the process of active dissolution was suspended. The anodic oxidation process is irreversible, since the reverse scan curve also had oxidation peaks accompanied by current oscillations, while reduction peaks were absent. Current oscillations were detected at potentials of thermodynamic possibility of oxygen release. It can be assumed that the released gas promoted the detachment of the oxide layer formed during direct unfolding, characterized by weak adhesion to the surface of the material.

After anodic polarization on the surface of the $n_5Si_{3-0.60}Ge_{0.60}$ electrode there was no visible layer of transformation products (Fig. 2). At magnifications of 370× and 1000×, it became clear that the most developed areas of the surface were cracks, where the manganese content was noticeably lower than in smooth areas, and the percentages of germanium and oxygen were higher. This allowed us to assume that the manganese silicide phase in this medium was stable and was not subjected to anodic destruction, while in the cracks, the transformation of manganese germanide with the ionization of manganese into a solution and the accumulation of insoluble germanium oxides occurred (Table 1).

The $Mn_5Si_{3-2.40}Ge_{2.40}$ material, containing a higher amount of germanium in the sample, was subjected to destruction at a significantly higher anodic current in the active dissolution region compared to $Mn_5Si_{3-0.60}Ge_{0.60}$ (Fig. 3). The process was also irreversible; the reverse curves for all cycles were above the forward curves, since

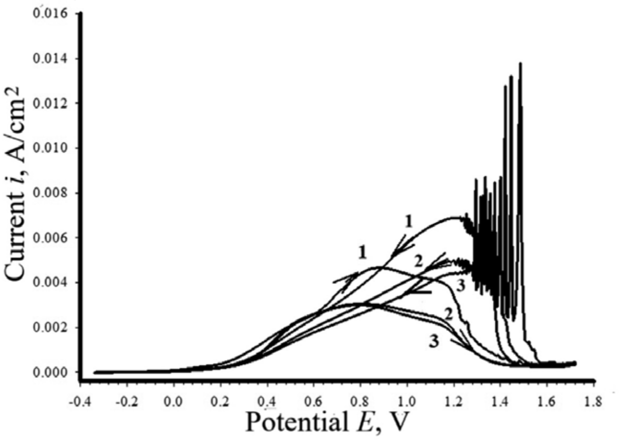

Fig. 1. Anodic CVA-curves for $Mn_5Si_{3-0.60}Ge_{0.60}$ in an 0.5M Na_2SO_4 solution, potential change rate is 5 mV/s; the number of the cycle is shown by a number near the curve

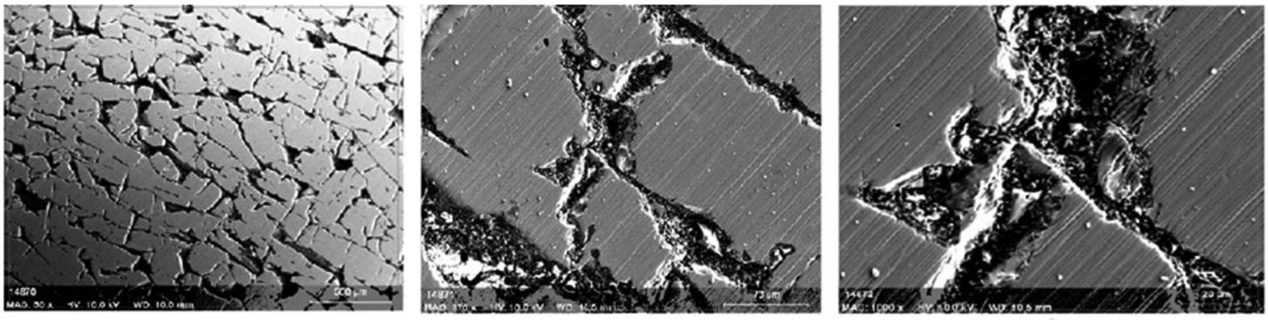
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Fig. 2. Micrographs of the $Mn_5Si_{3-0.60}Ge_{0.60}$ surface after 3 cycles of anodic polarization in an 0.5M Na_2SO_4 solution at the following magnifications: (a) 50×, (b) 370×, (c) 1000×

Table 1. Content of elements on $Mn_5Si_{3-0.60}Ge_{0.60}$ surface before and after anodic polarization

	ω_{at} Mn, %	ω_{at} Si, %	ω_{at} Ge, %	ω_{at} O, %
Surface before the polarization	60.25±2.55	31.24±1.87	6.16±0.83	2.35±0.51
On the surface	56.85±2.15	34.93±1.88	2.81±0.54	5.41±0.64
In the cracks	15.78±1.23	31.28±1.87	12.83±1.12	40.11±1.85

during reverse scanning, additional oxidation of components occurred on a more developed surface.

A yellow-brown oxide layer formed on manganese silicide germanide $Mn_5Si_{3-2.40}Ge_{2.40}$ during anodic polarization was clearly visible. Microscopic examination also showed the presence of a well-developed layer of anodic transformation products (Fig. 4). The layer was not continuous, it was loose, and easily detachable from the surface of the material. Uneven film formation led to current oscillations in the CVA curves (Fig. 3): during detachment, the current increased sharply and then decreased as a new portion of the product accumulated on the surface.

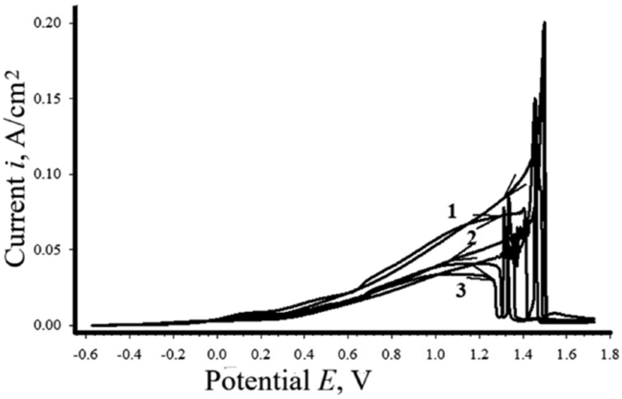

Fig. 3. Anodic CVA-curves for $Mn_5Si_{3-2.40}Ge_{2.40}$ in an 0.5 M Na_2SO_4 solution, potential change rate is 5 mV/s; the number of the cycle is shown by a number near the curve

Micro-X-ray spectral analysis of the surface showed that after anodic polarization the silicon content decreased slightly, the percentage of the manganese component decreased, and the germanium component increased. This suggested that the manganese silicide phase was still resistant to anodic destruction, manganese was actively removed into solution, and germanium remained on the surface in the form of yellow germanium oxide with complex composition GeO_X. In cracks, the composition of the anodic dissolution products differed from that on the sample surface, with a further depletion of manganese and enrichment of the germanium component.

The $Mn_5Si_{3-2.85}Ge_{2.85}$ sample consisted of 91 % of manganese germanide Mn_5Ge_3 phase, less thermodynamically stable during anodic oxidation in electrolyte solutions [11, 14]. Therefore, the currents in the active dissolution region were even higher than for $Mn_5Si_{3-0.60}Ge_{0.60}$ and $Mn_5Si_{3-2.40}Ge_{2.40}$ samples (Fig. 5). Oscillations associated with the detachment of anodic oxidation products were expressed less strongly; the reverse curve showed a sharp increase in current in active dissolution potentials, followed by a decrease. The process, just like in the previous samples, was not reversible; there was no symmetrical recovery peak.

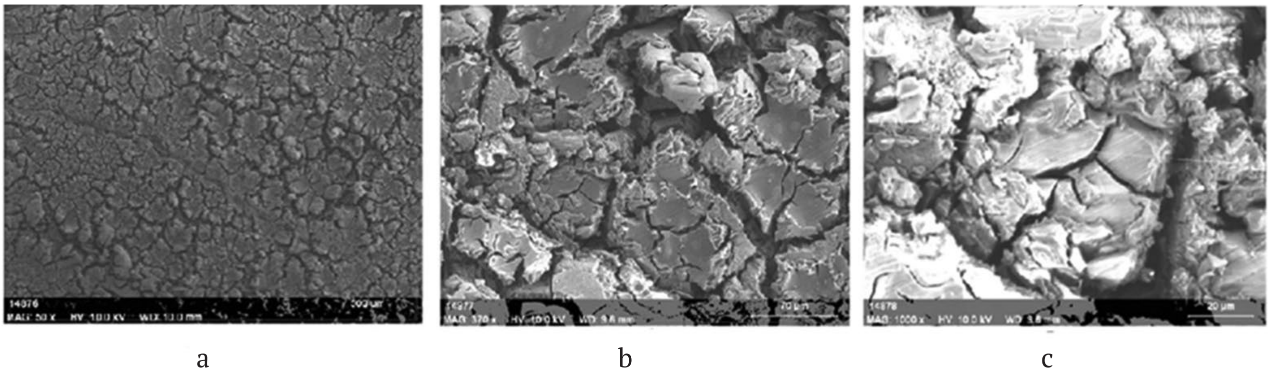

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Fig. 4. Micrographs of the $Mn_5Si_{3-2.40}Ge_{2.40}$ surface after 3 cycles of anodic polarization in an 0.5M Na_2SO_4 solution at the following magnifications: (a) 50×, (b) 370×, (c) 1000×

After anodic polarization in 0.5 M sodium sulfate solution on the surface of $Mn_5Si_{3-2.85}Ge_{2.85}$ similarly as on the surface of $Mn_5Si_{3-2.40}Ge_{2.40}$, the yellow-brown oxide layer was clearly visible. Surface microscopy demonstrated that this layer was even looser. At 2000x magnification, the smallest parts of the layer, represented by structures twisted into tubes became visible. The size of the particles that composed the oxide layer did not exceed several tens of micrometers (Fig. 6).

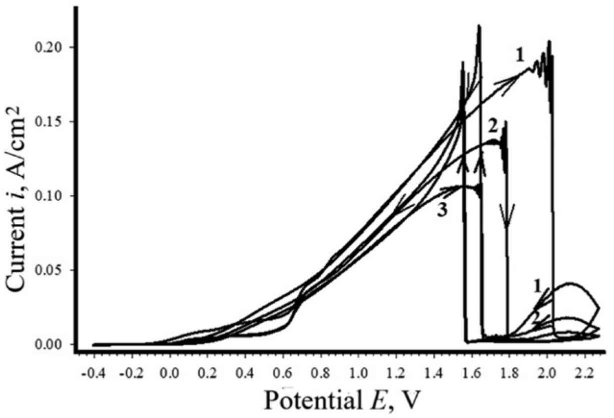

Fig. 5. Anodic CVA-curves for $Mn_5Si_{3-2.85}Ge_{2.85}$ in an 0.5 M Na_2SO_4 solution, potential change rate is 5 mV/s; the number of the cycle is shown by a number near the curve

Micro-X-ray spectral analysis showed a significant decrease in the content of manganese and silicon in the layer of anodic oxidation products and a simultaneous increase in the germanium and oxygen (Table 3). Apparently, the less thermodynamically stable phase of manganese germanide was destroyed with the transition of manganese into solution, leaving germanium oxide on the surface, characterized by poor adhesion to the surface and, consequently, a low protective effect.

The dried layer of anodic transformation products was easily separated from the sample by lightly tapping of the electrode on any hard surface. Micrographs of the cleaned surface are shown in Fig. 7. Surface relief of the $Mn_5Si_{3-2.85}Ge_{2.85}$ sample was quite developed, and areas affected by corrosion, where selective etching of manganese and the formation of oxides, primarily germanium

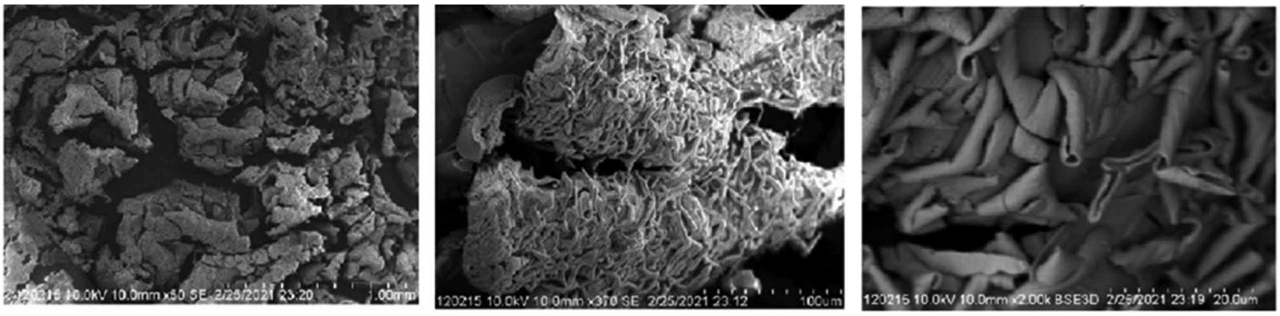

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Fig. 6. Micrographs of the $Mn_5Si_{3-2.85}Ge_{2.85}$ surface after 3 cycles of anodic polarization in an 0.5M Na_2SO_4 solution at the following magnifications: (a) 50×, (b) 370×, (c) 2000×

Table 2. Content of elements on the $Mn_5Si_{3-2.40}Ge_{2.40}$ surface before and after anodic polarization

	ω_{at} Mn, %	ω_{at} Si, %	ω_{at} Ge, %	ω_{at} O, %
Surface before the polarization	57.78±2.14	6.16±0.81	30.34±2.03	5.72±0.66
On the surface	20.13±1.93	5.97±0.79	47.07±2.12	26.83±1.64
In the cracks	11.79±2.25	5.65±1.79	53.49±3.34	29.07±2.73

Table 3. Content of elements on the $Mn_5Si_{3-2.85}Ge_{2.85}$ surface

	$\omega_{at.}$ % Mn	ω_{at} % Si	ω_{at} % Ge	ω_{at} % O
Surface before the polarization	61.34±2.15	3.27±0.08	30.51±1.75	4.88±0.53
The layer of the corrosion products	10.17±1.24	2.18±0.12	40.30±2.05	47.35±4.36
Cleaned surface	58.53±2.08	4.69±0.12	36.77±2.64	0

a b c

Fig. 7. Micrographs of the $Mn_5Si_{3-2.85}Ge_{2.85}$ surface after 3 cycles of anodic polarization in an 0.5M Na_2SO_4 solution, purified from anodic oxidation products at the following magnifications: (a) 50×, (b) 370×, (c) 2000×

oxides, occurred, were clearly visible. Micro-X-ray spectral analysis of the surface freed from oxidation products showed that quantitatively its composition was very close to the composition of the $Mn_5Si_{3-2.85}Ge_{2.85}$ surface before anodic polarization in a sodium sulfate solution (Table 3). A small increase in the fraction of silicon may indirectly indicate some enrichment of the surface with the manganese silicide phase Mn_5Si_3, while the upper surface layer of the manganese germanide phase Mn_5Ge_3 was completely transformed and removed.

3.1. X-ray phase and thermal analysis of anodic oxidation products

For more accurate determination of the composition of the corrosion products of germanium-containing phases, X-ray phase and thermal analysis methods were used. From among all materials studied, the powder detached from the $Mn_5Si_{3-2.85}Ge_{2.85}$ sample with the highest number of germanium atoms was chosen for further study.

The diffraction pattern of the anodic oxidation products removed from the surface of the sample is shown in Fig. 8. The absence of peaks and a large halo at small angles was characteristic for the presence of a large amount of amorphous phase and the absence of crystallites. This indicated the amorphous nature of the oxide layer formed during the corrosion process.

The results of thermal analysis of anodic oxidation products, thermogravimetric (TG) and differential scanning (DSC) curves are presented in Fig. 9.

On the TG curve, two processes of mass loss in the range of 100–600 °C and 650–1000 °C and the beginning of the melting process at 1137 °C were clearly visible. Mass spectrometric analysis revealed the presence of one water molecule in the compound, which evaporated during the first mass loss process. The second mass loss process corresponded to the phase transition of germanium monoxide GeO into germanium dioxide GeO_2. The DSC curve clearly showed the oxidation peak of GeO into GeO_2 at 1056 °C. The process involved the absorption of oxygen, as was indicated by the readings of the mass spectrometer. The onset of melting of the substance was recorded at 1137 °C. Considering that the melting of germanium dioxide is a relatively high-temperature process occurring at temperatures above 1137 °C, sublimation of the oxide onto the surface of the crucible can occur simultaneously, followed by the formation of refractory compounds [16]. After the analysis, it was noticed that the lid of the platinum crucible was tightly adhered to the crucible. When the

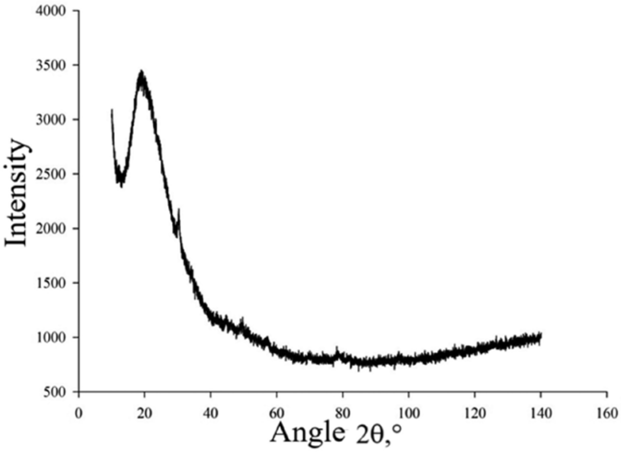

Fig. 8. Diffraction pattern of $Mn_5Si_{3-2.85}Ge_{2.85}$ anodic oxidation products

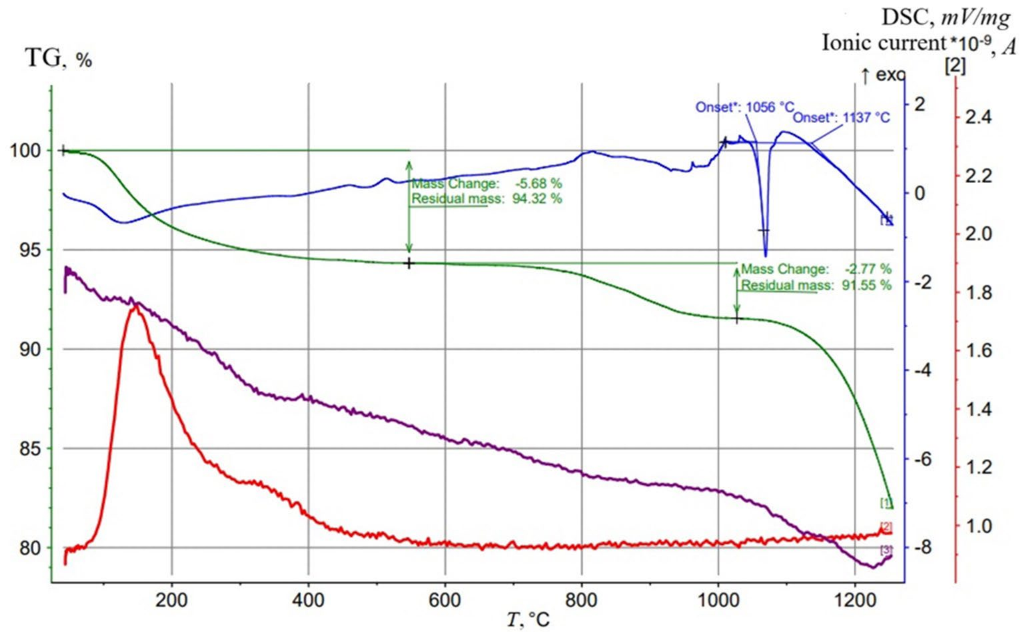

Fig. 9. Thermogravimetric and DSC curves for $Mn_5Si_{3-2.85}Ge_{2.85}$ anodic oxidation products

lid was removed, a thin film of reaction products could be detected. The weight of the crucible was also changed after thermal analysis. Thus, the corrosion products of the samples were predominantly oxygen-containing germanium compounds. Possible formulas of anodic oxidation products are GeO, GeO_2, and $Ge(OH)_x$.

4. Conclusions

Analysis of the CVA curves, the surface microstructure of the samples and their elemental composition after anodic oxidation showed that anodic destruction occurs selectively and predominantly affects the manganese germanide phase. In this case, manganese ionizes and passes into solution, and germanium forms an oxide layer containing GeO, GeO_2, and their hydrated form $Ge(OH)_x$ on the surface.

A comparison of changes in surface composition showed that with an increase in the fraction of germanium in manganese silicide-germanides, the ability of the material to resist anodic oxidation decreased. Thus, in the $Mn_5Si_{3-0.60}Ge_{0.60}$ sample with a high silicon and a low germanium content, after polarization, the fraction of the manganese component on the surface decreased by 6 %, while the germanium content decreased by half, and the fraction of silicon increased by 12 %. Corrosion products, mostly germanium oxides, accumulated in cracks. There was no visible oxide layer on the surface. This sample contained predominantly the Mn_5Si_3 phase, resistant to anodic oxidation in a wide range of aggressive media, and its behavior, including the absence of an abundant layer of products, was determined by it.

When the fraction of silicon in the sample decreased and the fraction of germanium increased to a composition of $Mn_5Si_{3-2.85}Ge_{2.85}$, the total amount of corrosion products increased, and they formed a developed layer of structures resembling microtubes, enriched in germanium oxide, which could be easily removed from the surface. Since this material contained predominantly the Mn_5Ge_3 phase, which did not exhibit high resistance to anodic destruction, its behavior was close to the behavior of the individual substance Mn_5Ge_3. In corrosion products, the fraction of manganese decreased by more than 80 %, silicon by 33 %, and the fraction of germanium increased by 32 %. The surface under the product layer also underwent changes: manganese was selectively etched from it, its fraction decreased by 5 %, while the fraction of germanium increased by 20 %, and silicon by 43 %.

Changes in the content of components the sample of intermediate $Mn_5Si_{3-2.40}Ge_{2.40}$ composition was due to the behavior of both phases: Mn_5Si_3, and Mn_5Ge_3. The product layer was sufficiently formed, but it was bound to the surface more strongly than in the case of $Mn_5Si_{3-2.85}Ge_{2.85}$. The manganese content in the products was 65 % lower than in the original material, and the germanium content increased by 5 5%. The fraction of silicon changed insignificantly. Most of the oxidation products were contained in cracks, where the fraction of germanium was 76 % higher than on the original surface.

Thus, the active transition of the manganese germanide phase into solution enriches the surface of the sample with a silicide phase that is more resistant to anodic oxidation.

Contribution of the authors

The authors contributed equally to this article.

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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