Physical Chemistry

INORGANICANTISUBLIMATION MATERIAL FORTHERMOBATTERIES BRANCHES BASED ON SIGE ALLOYS

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ABSTRACT. *Polycrystalline SiGe alloys are high-temperature thermoelectric materials and are widely used for production of p- and n-branches of thermoelectric batteries, with working temperature above 1000^0C. At these temperatures evaporation of germanium and dopant materials (boron and phosphorus) takes place from SiGe alloys. This process might stipulate worsening thermoelectric characteristics of the thermoelectric converter and decreasing duration of its working resource. This highlights the need for the formation of antisublimation coatings on the surface of the thermoelements branches, compatible in their physical-chemical properties with their characteristics.*

In practice, silicon nitride and high-temperature organic and inorganic materials are widely used to solve this problem. This is stipulated by the presence of relatively simple technological processes of their creation and practical application. These materials are characterized by high brittleness or become brittle during operation of the thermobatteries at high temperatures. In case of organic materials liquid hydrocarbons are additionally released, which form carbon at high temperatures. As a consequence, the electrical insulating characteristics of thermobatteries deteriorate, which often leads to a short circuit. In the process of operation of thermobatteries, both planned and unplanned changes in temperature often take place. It can cause damage to the continuity of a thin layer of protective coating.

Hightemperatureelectroinsulatingantisublimation coatings based on vitreous enamels have been created by us for protecting p- and n-types branches of thermoelements based on SiGe. By varying the chemical composition of the glass frit, vitreous enamel has been obtained, that meets the requirements for the physical-chemical properties of antisublimation coatings at temperatures of 1000-1100°C.

The following chemical composition of glass frit: Na_2O-K_2O-ZnO-Cr_2O_3-Al_2O_3-SiO_2 was developed based on liquid glass Na_2O•n SiO_2. Based on these materials, high-temperature antisublimation coatings of the highest quality are formed on the surface of p- and n-branches of SiGethermoelements. The proposed material can preserve the strength of the connection of the branches of thermoelements at the initial level, their electrical insulation and antisublimation properties in case of temperature change of the thermoelectric generator at a speed of 100^0C C/min in the temperature interval of 1000-25^0C.

Key words: *thermoelectric battery, thermoelement, silicon, germanium, glass frit.*

SiGe alloys, doped by phosphorus or boron are highefficient thermoelectric materials and have wide application in thermoelectric instrument-making for various purposes. In particular, they are used for manufacturing n- and p-branches of hightemperature thermoelectric batteries (TB). However, at the working temperature of 1000°C and above pointed alloy is characterized by noticeable volatility of Geand especially alloying additives of PandB [1]. In this regard, it is necessary to create preliminarily antisublimation coatings on the surface of thermoelements branches (TE). In practice, it is widely used silicon nitride, Al_2O_3 with an organically bonding material [2], organosiliconmaterials [3,4]. The selection of these materials due to their high thermal stability, radiation resistance, moisture resistance, good adhesion to the substrate and manufacturability [5].The disadvantages of these materials is that they are characterized by high brittlenessor they become brittle during operation at high temperatures. This process leads to the thermomechanical stresses in the volume of thermoelectric branches, which in turn leads to disruption of the integrity of the brittle layer of the protective coating,that causes significant decrease of antisublimation characteristics.In case of coatings made from organic and organosilicon materials, an additional disadvantage is that at operating temperatures of TB (1000-1100°C), hydrocarbons are excreted in the form of methane (CH_4), benzene (C_6H_6) and other organic compounds[4]. If these compounds get into the high temperature zone of thermoelectric generator (TEG) their pyrolysis takes place with the excretion of carbon, which penetrates into the insulating nodes and leads to a deterioration of its insulating characteristics, up to a short circuit [6]. This process, in turn, causes a significant decrease in the exploitation resource of expensive electric power installation. Based on the noted shortcomings of the known protective coatings for thermoelectric branches and physical-chemical and thermal-physical characteristics of glass frit, the possibility of creating an anti-sublimation electrically-insulating coating from inorganic vitreous enamel for n- and p-types branches based on SiGe were investigated.

It is stipulated by the fact, that different systems of glass frit allow to obtain vitreous enamel coatings for temperature interval of 1000-1100^{0}C with given physical-mechanical characteristics. However, the created material, with the above mentioned characteristics should be connecting material of thermoelements branches and allow the installation of thermobattery at room temperature. For solution of this problem, the most suitable material isnatriumliquid glass (Sodium silicate) – $Na_2O \cdot n\ SiO_2$, which consists of Na_2O, SiO_2, $H_2O$and is characterized with density of 1,30-1,45 g/cm^3 [7]. Use of this material is stipulated by its connecting possibility at room temperature, and when heated to 100-120^{0}Cin an air atmospherein places of connection of samples vitreous enamel layer is formed [8]. Despite this, liquid enamel cannot be applied to solve this problem without hightemperature fillers. Therefore, considering the physical-chemical properties of metal oxides and necessity of having low values of coefficient of thermal expansion, thermal conductivity, high electrical insulating properties of created material, following materials were selected as fillers to liquid glass: Al_2O_3,B_2O_3,Cr_2O_3, $K_2Cr_2O_7$ (anhydrous), ZnO, BaO, PbO. In all cases chemical interaction with surface of SiGe samples mixtures of these metal oxides with Na_2O and SiO_2 was investigated. The quantitative content of the last oxides in all cases was the same and was determined by their content in the liquid glass. Results are presented in Table 1.

Based on data from Table 1, multicomponent systems of glass frit werecomposed andtheir basic properties were determined by theoretical calculations [9-10]. The results of the calculation are shown in Table 2.

Results of chemical interaction with the surface of SiGe branches of thermoelementand quality of formed coatings (t=900 ^{0}C, T=1 hr., environment - air)

Table 1

№ Content	Material		State of formed coatings
	Metal oxide	Metal oxide+liquid glass	
1	Al_2O_3	$Na_2O \cdot Al_2O_3 \cdot SiO_2$	Weak roughness, weak adhesion, coating similar to ceramic
2	Cr_2O_3	$Na_2O \cdot Cr_2O_3 \cdot SiO_2$	Glass coating,good adhesion to the substrate
3	B_2O_3	$Na_2O \cdot B_2O_3 \cdot SiO_2$	A thin layer of low-melting vitreous-enamel coating is formed
4	$K_2Cr_2O_7$	Homogeneous slip is not formed	Does not interact chemically, the coating is not formed
5	BaO	$Na_2O \cdot BaO \cdot SiO_2$	Rough-porous coating with weak adhesion to the substrate is formed
6	ZnO	$Na_2O \cdot ZnO \cdot SiO_2$	Vitreous enamel coating with smooth surface is formed with liquid glass , good adhesion to the substrate
7	PbO	$Na_2O \cdot PbO \cdot SiO_2$	A very thin layer of coating with pores is formed

Selected systems of glass frit and their properties

Table 2

№ Sys-tems	Components of the composition	Properties				
		Melting tempera-ture, ^{0}C	Thermal conducti-vity, Cal/cm.sec, ^{0}C	Coefficient of thermal expansion, 10^6deg^{-1}	Tensile strength, kg/cm^2	Electrical resistance, Ohm.cm
1	Na_2O-ZnO-Al_2O_3-SiO_2	1055	0,0015	3,9	117,0	10^4-10^{12}
2	Na_2O-Al_2O_3-Cr_2O_3-SiO_2	1220	0,0013	3,3	138,8	
3	Na_2O-K_2O-Al_2O_3-SiO_2	845	0,0010	>14,0	106,9	
4	Na_2O-ZnO-Cr_2O_3-BaO-SiO_2	843	0,0020	8,1	98,8	
5	Na_2O-K_2O-Cr_2O_3-Al_2O_3-ZnO-SiO_2	1150-1200	0,0016	6,2	126,9	

Table 2 shows, that coefficient of thermal expansion, thermal conductivity and tensile strength of almost all coatingsfrom the given system of glass frit might be used as a protective coating of thermoelectric based on SiGe. However, based on the working temperature of thermobattery, which is 1000-1100°C and the need for a "soft" state of the antisublimation coating at this temperature, glass frit of the system #5 with melting temperature 1150-1200^{0}C was selected as a high-temperature antisublimation-electro insulating coating of thermoelectric branches. This was due to the fact that, at pointed working temperature TBvitreous –enamel coating based on system #5 (Table 2) will not be in a fragile state, as ceramics and other high-temperature electro-insulating materials , but is a “soft” state. This in turn significantly reduces sublimation of thermoelectric material at given working temperature of thermobattery, in a long time work as well aswith repeated planned and forced thermal cycling. This is confirmed by the fact that the vitreous enamel slip made from components, contained in the system glass frit №5 (Table 2), deposited on the surface of p- and n-types branches of thermoelements, after preliminary thermal treatment by the found regime (fig. 1) [7], forms an antisublimation glass-enamel coating, which fully withstands all subsequent technological operations for preparation of branches of thermoelements and the creation ofthermobatteryby diffusion welding.

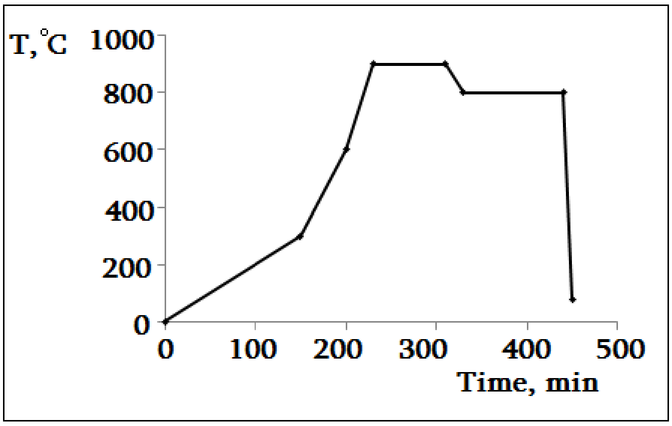

Fig. 1.Temperature regime of formation of glass-enamel coating

Formed coating with thickness 0,05-0,1 mm, is an electrical insulator and has tensile strenght >80 kg/cm^2, which is retained after repeated thermal cycling at a heating-cooling speed ≈100^{0}C/minin temperature interval of 1000-25^{0}C (Fig. 2) without formation of visible defects or other types rejects on the surface layer of the coating.

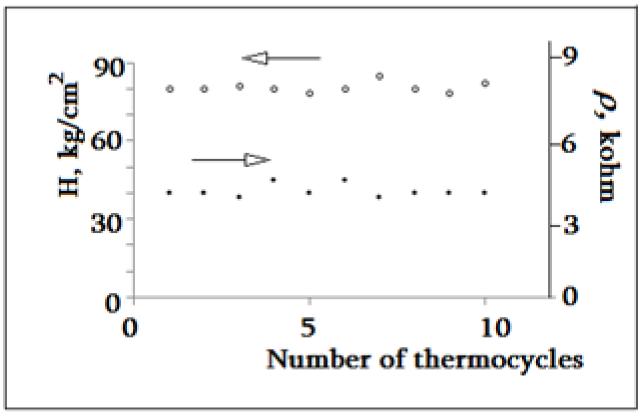

Fig. 2. Changes of glass-coating properties depending on the number of thermal cycles

Therefore, glass frit with following components Na_2O-K_2O-Cr_2O_3-Al_2O_3-ZnO-SiO_2 was selectedfor further investigation and creation of optimal chemical composition of glass frit and vitreous enamel antisublimation coating on its base for SiGe thermoelectric branches.

It is shown, thatvitreous enamel based on the selected system of glass frit provides a strong adhesion of the surface of thermoelectric branches with defect-free anti-sublimation coatings, which retains these characteristics with multiple thermal cycling, at a speed of ≈100^{0}C/minin temperature interval of 1000-25^{0}C.

Achieving high quality vitreous enamel coating is stipulated by physical-chemical properties of liquid glass and correct selection of content of glass frit system.

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