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Thin-Film Coatings Based on Hollow Inorganic Microsheres and Polyacrylic Binder

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Abstract
This article presents a study of thermal, mechanical-and-physical properties of heat-insulation materials based on hollow inorganic microspheres bonded by polyacrylic binder. The calculated and experimental values of thermal conductivity coefficient of thin-film heat-insulation coatings with acrylic binder were obtained at 25^0C. Hollow glass and ceramic microspheres were used as coating filler. Studies have shown that the actual values of thermal conductivity coefficient of heat-insulation coatings with hollow micro-spherical filler vary within the range of 0.10-0.18 W/(m·K). The study on the specific heat capacity of thin-film heat-insulation coatings have shown that heat capacity of thin-film insulation coatings increases with increase in temperature, thereby reducing the heat transfer coefficient and improving in general material's insulating properties. The determination of the linear thermal expansion coefficient of the thin-film heat-insulation coatings was conducted depending on the binding content and external temperature. It is revealed that the decrease in the binder content regardless of the external temperature leads to a decrease in the linear thermal expansion coefficient due to the dominance of the glass phase in the composition.

Key words: spheroplastics, polyacrylic binder, hollow glass and ceramic microspheres, thin-film heat-insulation coatings, heat resistance, thermal conductivity coefficient, linear thermal expansion coefficient.

INTRODUCTION

To date spheroplastics, which are spherical fillers bonded by the polymer matrix, became widespread in all industrialized countries. Thin-film heat-insulation coatings (thin-film HIC), which are composite materials where the hollow microspheres are bonded with polymer binder, are one of the varieties of spheroplastics [1-3]. Due to the presence of the gas phase, they are characterized by reduced thermal conductivity coefficient and occupy a significant place in the development of new insulation materials. The availability of hollow particles provides a low density, increased strength, and reduced linear thermal expansion coefficient (LTEC). The selection of the binder largely determines mechanical-and-physical as well as thermal properties of thin-film HIC. Currently, much attention is paid to thin-film HIC based on polyacrylic binders, due to their acceptable thermal stability, environmental safety, and the possibility of curing at room temperatures [4-6]. Almost all heat insulation compositions with operational temperature up to 100^0C produced in the Russian Federation have similar composition consisting of acrylic water dispersion, hollow microspheres, and a small amount of modifiers, practically having no effect on heat transfer. However, according to many specialists in heat engineering, thermal and physical characteristics provided by manufacturers are overestimated [7].
The aim of the present work was to study the actual thermal-physical and mechanical characteristics of thin-film heat-insulation coatings from the group of polyacrylic water dispersion binders, and glass and ceramic hollow microspheres, as well as the possibility of using these compositions for heat insulation of conduits and chemical production facility.

RESEARCH OBJECTS AND METHODS

The most common acrylic water dispersion MBM-5C, which is the acrylic copolymer produced by LLC "Kurskkhimprom" (Kursk) according to TU 6-01-274-79, was used as a binder.
Hollow glass microspheres MS-A9 (group A1 TU 6-48-108-94), which are an inert spherical particles filled with air with the average particle size of 30-60 μm, and hollow ceramic microspheres produced by flotation of smoke emissions of solid fuel fired thermal power plants (operating on coal from Kuznetsk coal basin), were used as hollow microspheres. Figure 1 shows a micrograph of hollow glass microspheres, which were used in the research.

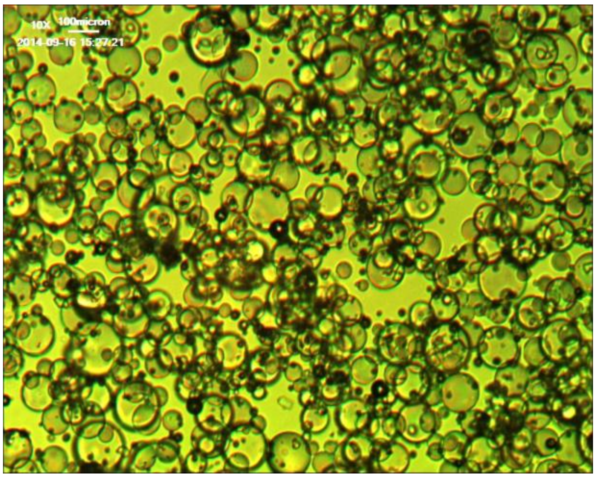

Figure 1. Hollow glass microspheres.

Samples of thin-film HIC with content of binder up to 50% (by volume) were obtained by mixing a predetermined amount of binder and microspheres, and applying further a layer of the composition on the substrate using a palette-knife, followed by curing the samples at room temperature for 72 hours.

Thermal conductivity coefficient was determined in a dynamic mode according to GOST 23630.2-79 using the IT-λ-400 instrument.

Specific heat capacity was determined according to GOST 23630.1-79 using the IT-C-400 instrument, while linear thermal expansion coefficient (LTEC) was measured with the use of quartz dilatometer according to GOST 15173-70.

RESULTS AND DISCUSSION

Thermophysical properties of insulation materials are dependent on proportion of binder and filler, as well as their nature. Thermal conductivity of composite heat-insulation materials consisting of several components can be found using the following dependence [5,8]:

$$\lambda = \lambda_{св.}(1-\varphi) + \lambda_{н}\varphi$$

where λ – is the thermal conductivity of the multicomponent material;

$\lambda_{св.}$, $\lambda_{н.}$ – are thermal conductivities of the first and second components;

φ – is the volume fraction of filler.

The calculations were performed taking into account that experimentally determined actual thermal conductivity of glass and ceramic microspheres is 0.089 and 0.134 W/(m·K), respectively.

Tables 1 and 2 present the calculated and experimental values of thermal conductivity coefficient of thin-film HIC with acrylic binder at 25°C, where hollow glass and ceramic microspheres were used respectively as filler.

In general, the calculated and experimental data are close enough. Deviations can be explained due to the availability of hygroscopic moisture. Figure 2 shows the temperature dependences of thin-film HIC with various fillings. The increased value of thermal conductivity of binder compared to the same organic materials is due to the relatively high flexibility of macromolecules associated with low intermolecular interaction of the chains. As is shown in Fig.2, at the volume fraction of the binder equal to 50%, heat conductivity coefficient slightly depends on temperature within the range of 20-100^{0}C.

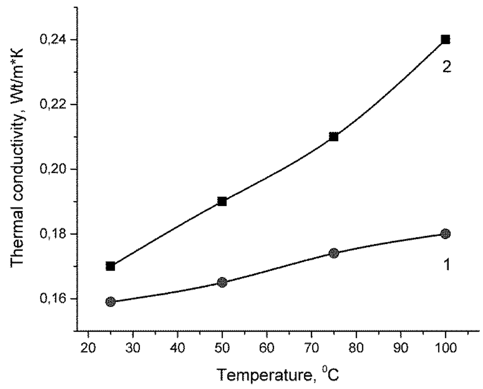

Figure 2. Temperature dependence of thin-film HIC with glass (curve 1) and ceramic (curve 2) microspheres (50% of the binder).

Table 1. Thermal conductivity of thin-film HIC based on hollow glass microspheres at 25^{0}C

Binder content, % (by volume)	Material density, kg/m^3	Thermal conductivity coefficient of thin-film HIC W/m·K	
		Calculated value	Experimental value
30	388	0.114	0.127
50	453	0.136	0.144
70	795	0.164	0.170
100	1080	0.21	0.21

Table 2. Thermal conductivity of thin-film HIC based on hollow ceramic microspheres at 25^{0}C

Binder content, % (by volume)	Material density, kg/m^3	Thermal conductivity coefficient of thin-film HIC W/m·K	
		Calculated value	Experimental value
30	482	0.146	0.159
50	573	0.176	0.180
70	805	0.184	0.184
100	1080	0.21	0.21

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Similarly to the previous case, heat capacity of thin-film HIC with a polyacrylic binder is largely dependent on components proportion. High heat capacity of the pure acrylic polymer (curve 1) is due to the substantial mobility of polymer macromolecule segments and weak intermolecular interaction. The same applies to compositions with a high content. Since the heat capacity of acrylic polymer is significantly higher than that of the glass, reduction in the volume fraction of the binder in thin-film HIC to 10% leads to a decrease in heat capacity down to the minimum value (1050 J/kg·K).

Heat capacity of substances is determined by molecules degree of freedom. With increase in temperature the mobility of molecules in components increases and respectively heat capacity of thin-film HIC increases as well (Fig.3), especially for compositions with a high content of binder.

In general, we must take into account that the increased heat capacity of the composition contributes to the reduction of heat transfer coefficient that in general improves heat-insulation properties of thin-film HIC.

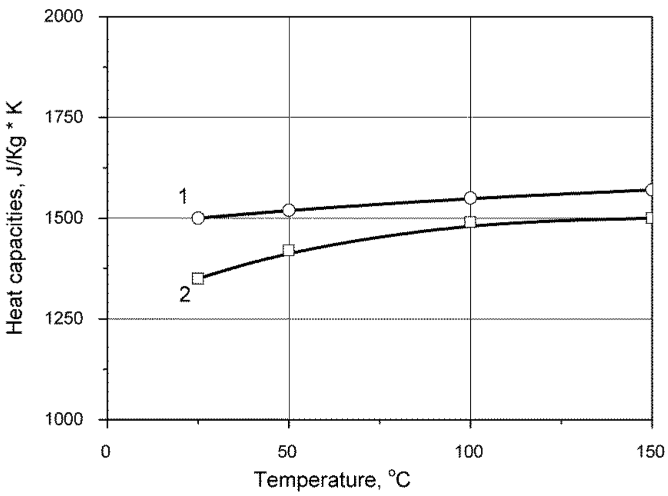

Figure 3. Specific heat capacity of the thin-film HIC versus temperature (curve 1 – glass spheres, curve 2 - ceramic spheres)

The role of the linear thermal expansion coefficient (LTEC) of composite materials is quite significant, because even minor differences in LTEC of the composite material components causes stresses that can lead to the formation of microcracks and partial destruction. Accordingly, at the next phase of the work we have carried out studies on the determination of the linear thermal expansion coefficient of thin-film HIC depending on the content of binder and external temperature.

The linear thermal expansion coefficient is largely influenced by the volume fraction of the binder contained in the thin-film HIC (Fig.4).

In general, most polymers are characterized by high values of LTEC of the acrylic polymer. The decrease in the content of the binder leads to a decrease in LTEC regardless of the external temperature due to the dominance of the glass phase in the composition. At the binder volume fraction of 10% the values of LTEC decrease by an order compared to unfilled polymer. At that, there is the possibility to achieve the necessary values of LTEC by adjusting the ratio between filler and binder. This is very important when using the thin-film HIC for composite coatings, where significant differences in LTEC can lead to deformation, and sometimes the destruction of insulation.

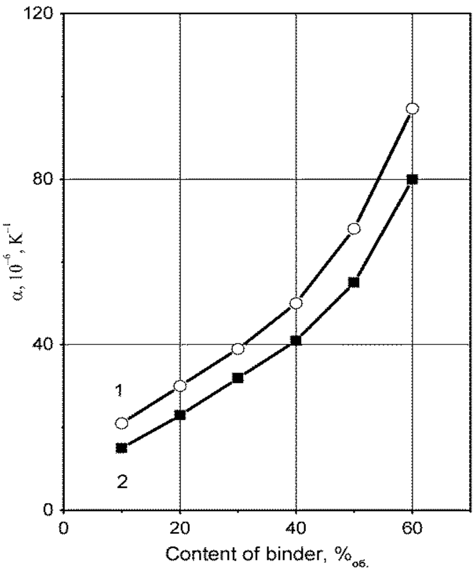

Figure 4. The linear thermal expansion coefficient (LTEC) versus content of the binder in thin-film HIC (curve 1 – glass spheres, curve 2 – ceramic spheres).

Conducted studies have shown that the actual thermal conductivity coefficient of heat insulation coatings with hollow microsphere fillers varies within the range of 0.1-0.18 W/(m·K).

Thus, thermophysical characteristics of most of the heat-insulation coatings produced by the Russian manufacturers are overestimated, and thus we will use the obtained experimental data in subsequent thermal design.

However, in spite of a partial discrepancy of thermophysical characteristics declared by producers and calculated by heating engineers, thin-film HIC has a distinct advantage over heat-insulation materials such as for example fiberglass and foam glass. This advantage is weak dependence of the thermophysical characteristics on external effects, ease of applying the product of any complexity, high mechanical strength allowing dispensing with external shielding, good decorative properties, resistance to external effects, as well as the constancy of thermal characteristics throughout the entire lifetime.

THERMAL CALCULATION OF INSULATION

Thermal calculation of insulation usually requires:

a) defining required thickness of the core layer of the insulation structure based on the predetermined (standardized) heat losses;

b) defining heat losses in the heat conduit at the known design of the heat insulation blanket and its main layer thickness.

Since the calculation of the heat insulation thickness has no analytic solution and is carried out based on time-consuming numerical methods, to automate calculations, the solution of the heat transfer problem was carried out by means of MathCAD 15 using the built-in Given and Find functions, as well as programming tools using SNiP 41-03-2003 "Heat insulation of the facility and conduits". The solution comes down to finding thickness of the insulation at prescribed convection and radiation losses.

The example of thickness calculation of thin-film HIC with an acrylic binder and hollow glass microspheres is given below and shown in Fig.5. The calculation was carried out using the MathCAD 15 mathematical package. Calculation algorithms and code listings are given in [9, 10].

Initial data for the calculation of thin-film HIC thickness according to the code listing (Fig.4):

The temperature in the conduit, T_{in} = 95℃;
The out-to-out diameter of the conduit, DN = 0.219 m;
The insulation surface temperature, T_{out} = 45 ℃;
Ambient temperature, T_{oc} = 20 ℃;
Thermal conductivity coefficient, λ=0.1 -0.2 W/(m·K):

The standardized heat transfer coefficient due to convection and radiation from the outer surface of the insulation σ, W/(m²·K), is selected for the devices located indoor according to SNiP 2.04.14-88 "Heat insulation of the facility and conduits". Based on this σ = 35 W/(m²·K).

Table 3 presents thicknesses of the polyacrylic thin-film HIC depending on thermal conductivity. Data are obtained by thermal design according to the code listing shown in Fig.5 based on the use of Windows 10 and MathCAD 15 operating system.

Listing

Thermal design was performed according to the procedure expounded by the code of
Practice SP 61.13330.20012 "Heat insulation of the facility and conduits".
Revised edition SNiP 41-03-2003.

Basic data:

Temperature in conduit °C
$T_{in} = 95;$
Out-to-out diameter of conduit, m
DN = 0.219 m;
Heat-insulation surface temperature, °C
$T_{out} = 45;$
Ambient temperature, °C
$T_{oc} = 20;$
Mean temperature of the layer, °C

$$O_{cp} := \frac{(T_{in} + T_{out})}{2}$$

Thermal conductivity coefficient, W/(m K)
$O_{cp} := 70;$
Convection and radiation losses from outer surface of heat insulator, W/(m² K)
$\sigma := 35;$
Specified thickness of heat insulator layer, m
$\delta := 0.02;$

Determination:

To define heat-insulation layer thickness we conducted iterative search using the built-in *Given* and *Find* functions

Given

$$\frac{\ln\left(\frac{DN + 2 \cdot \delta}{DN}\right) \cdot \sigma \cdot (DN + 2 \cdot \delta)}{2 \cdot \lambda} = \frac{T_{in} - T_{out}}{T_{out} - T_{oc}}$$

Effective thickness of insulation blanket, m
$\delta r := Find(\delta) = 5.57\ x\ 10^{-3}$

Figure 5. Code listing to design the insulation blanket thickness.

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Table 3. Calculated thickness of heat-insulation coating

Thermal conductivity coefficient, λ, W/(m^2·K)	Thickness, mm
0.1	5.57
0.125	6.92
0.15	8.26
0.175	9.59
0.200	11.00

When studying mechanical-and-physical properties and obtaining experimental batches of thin-film HIC, we used a filler with conventional fractional composition, because change in the fractional composition of hollow glass microspheres is economically unviable due to their high cost, as well as ineffective from a technical point of view.

When loading of filler into the polymer, the tensile strength of material increases (Fig. 6). This can be explained using the model of elastomer molecules slippage along the filler surface (Denneberg model [11]).

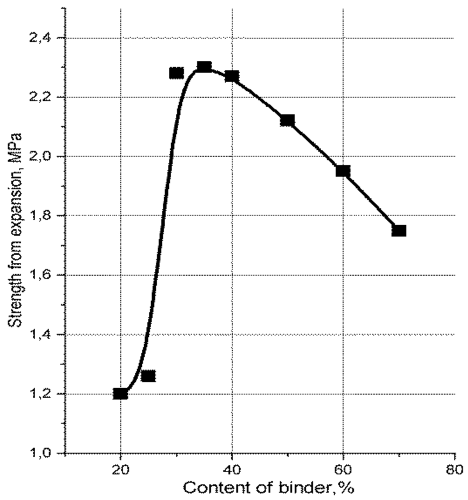

Figure 6. Tensile strength of the heat-insulation coating versus the content of polyacrylic binder with hollow glass microspheres.

The lack of filler initiates rupture of short chains, while presence of filler increases the number of loaded chains that consequently leads to a redistribution of the load. The decrease in volume fraction of the binder below 30% causes a sharp decrease of tensile strength of the thin-film HIC due to deficiency of the binder. In addition, the amplification effect is possible also due to the formation of chemical bonds between the binder and filler, for example, between active groups of the binder and silanol groups on the surface of the glass filler.

Given the fact that the composition of the studied model system practically does not differ from the compositions available in the domestic market, the technology of applying thin-film HIC based on polyacrylic binder, which is filled with hollow microspheres, is quite simple and versatile.

When insulating objects with a simple shape, application of the insulating material can be done using a roller or palette-knife. When insulating complex shapes, it is appropriate to apply layer-by-layer coating using any type of spray diffusers suitable for high-viscosity media. Technological modes of spray diffuser operation and subsequent drying of the thin-film HIC are defined by the manufacturer.

The application of all acrylic heat-insulation materials on facility and conduits is carried out uniformly according to the standard scheme.

The working surface must be dry and clean. It is recommended to prime metal surface with proper primer. The consumption of insulating material is 400 g/m^2. Insulation layer thickness should be at least 1-1.5 mm. The material is applied by means of spray gun in several layers with intermediate drying for 2 hours until reaching the specified thickness. The dry to touch time is 1 hour, while full drying under normal conditions takes 24 hours.

Thus, obtaining the coating blanket noted in the example and providing required thickness of the thin-film HIC will need in average application of four layers of material that can be done within one working day.

CONCLUSIONS

1. Thin-film heat-insulation coatings based on polyacrylic binders have acceptable thermal stability (up to 100^0C), environmental safety and the ability to cure at room temperature;
2. According to the conducted research results, the actual thermal conductivity coefficient of thin-film heat-insulation coatings based on polyacrylic emulsions and glass microspheres ranges from 0.10 to 0.18 W/(m K);
3. The use of hollow ceramic microspheres degrades the insulating properties of thin-film coatings;
4. Thin-film heat-insulation coating application technology allows insulating conduits, reservoirs, tanks, containers, and other chemical production facilities;
5. To obtain the necessary heat-insulation characteristics when using these coatings, the thickness of the polyacrylic thin-film heat-insulation coating must be at least 5 mm (that requires application of 4 layers of material at each layer thickness of 1-1.5 mm).

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