ISSN 1070-4272, Russian Journal of Applied Chemistry, 2014, Vol. 87, No. 10, pp. 1430−1434. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © M.P. Krasnovskih, N. G. Maksimovich, Ya. I. Vaisman, A.A. Ketov, 2014, published in Zhurnal Prikladnoi Khimii, 2014, Vol. 87, No. 10, pp. 1421−1428.

Thermal Stability of Mineral-Wool Heat-Insulating Materials

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Received November 14, 2014

Abstract—When mineral wool articles are heated, organic compounds are released into the gas phase due to the pyrolysis of the polymer binder beginning at 240°C. There are two temperature ranges of pyrolysis: mostly oxygen-free hydrocarbons are observed in the products below 400°C, and oxygen-containing hydrocarbons, above this temperature, in the case of an oxidizing atmosphere. Mineral wool articles contain more than 5 wt % polymer binder. Aluminosilicate fibers have amorphous structure and crystallize into the augite phase when heated to above 850°C.

DOI: 10.1134/S1070427214100061

Artificial mineral fibers are widely used to manufacture heat-insulating and acoustic articles. The overall production of materials and articles based on artificial mineral fibers constitutes a considerable part in the production of heat-insulating and acoustic materials of all kinds. Heat-insulating articles based on mineral fibers make it possible to create various kinds of light-weight constructions. For example, use of panel enclosures with mineral-wool plates as thermal insulation makes it possible to reduce, compared with the standard reinforced-concrete components, the mass of the main construction elements by a factor of 4–5, and the labor input for erection of buildings, by a factor of 1.8–2, with the construction period becoming substantially shorter [1].

There is a tendency all over the world toward an increase in the manufacture of mineral-wool heat-insulating materials, which is due to the rise in the capital development of energy-saving building projects and to the improvement of their performance characteristics.

The basic property of mineral wool is its high heat- and sound-insulating capacity, stability against temperature deformations, poor moisture absorption, chemical and biological resistance, and ease of assembly. A mineral-wool heat insulator is a chemically inert medium and does not cause any corrosion of contacting metals.

Mineral wool is manufactured from the following materials: rock of gabbro-basalt type and analogs of these; sedimentary rock; slaggy lava; industrial wastes, including break stone produced from blast-furnace slag; as well as mixtures of the above components and other raw materials from which a stock of acceptable composition can be obtained and, further, high-quality wool [2]. For example, basalt fibers are manufactured from basalt rock of volcanic origin, which has good thermal properties and chemical resistance. The main constituents of basalt are silicon, aluminum, iron, calcium, and potassium oxides [3]. To impart rigidity to finished articles, binders are added in the course of their fabrication. As binders serve polymers that preclude free displacement of fibers with respect to each other and fix the structure of an article. Thus, finished mineral-wool articles are composite materials containing a polymer binder in addition to the silicate fibers proper. The technical requirements to mineral-wool articles are presented in GOST (State Standard) 4640–93 “Mineral wool.”

Because of the complex composition of mineral-wool articles, their thermal treatment both in service and in emergencies may give rise to a number of processes leading to disintegration of a material or its components and yielding products affecting the environment. This

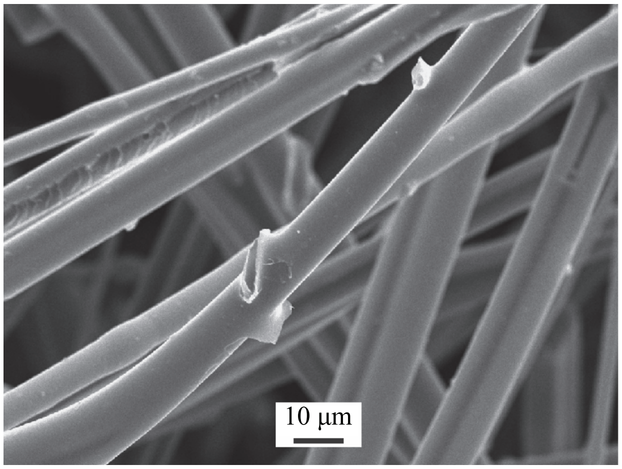

Fig. 1. SEM image of a mineral-wool heat-insulating material.

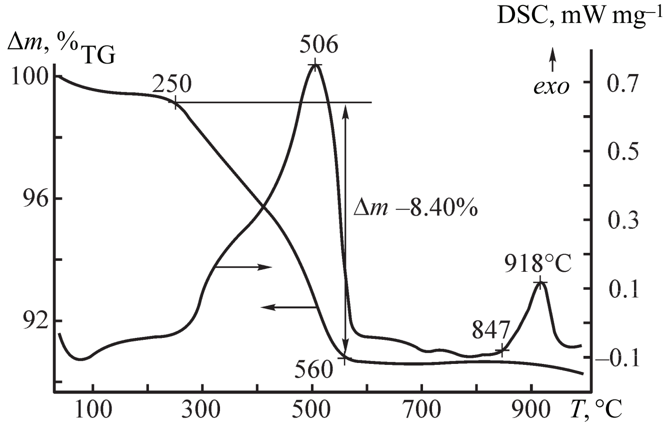

Fig. 2. Results furnished by a thermogravimetric analysis of a mineral-wool sample and by differential scanning calorimetry DSC. (Δ*m*) Loss of mass and (*T*) temperature.

circumstance is particularly critical when mineral-wool articles are used for heat insulation of technological apparatus and pipelines.

In the present study, we examined the thermal impact on mineral-wool articles by scanning electron microscopy, X-ray phase analysis, and thermogravimetric mass spectrometry.

EXPERIMENTAL

We examined two types of industrially manufactured mineral-wool articles, those based on gabbro-basalt rock and slags. A thermogravimetric analysis was made with an STA 449 F1 synchronous thermal analysis instrument (Netzsch, Germany), which enables a thermal study of a sample, with its thermogravimetric and calorimetric characteristics simultaneously recorded. The gaseous products released in the process were analyzed with a QMS 303 CF Aeolos mass spectrometer (Germany). The results obtained were processed using the software shipped with the corresponding instruments. An X-ray phase analysis was made with a D8 Advance diffractometer (Bruker, Germany) with CuK_α radiation.

The results of scanning electron microscopy (SEM) demonstrated that all the samples contain a binder that covers the surface of fibers and forms aggregations at intersection of fibers (Fig. 1). It can be seen in Fig. 1 that all the samples contain a polymeric additive to mineral fibers and its flaking in the central part of the image suggests that the whole visible surface of the fibers is covered with a film of this kind. It is clearly seen that there is the polymer at the place of contact between two fibers, with these combined by the binder at considerable distances.

This amount of the polymer in a sample means that the regulatory standard defined by GOST 4640–93 is exceeded. Indeed, a thermogravimetric analysis of a mineral-wool sample based on fibers produced from gabbro-basalt rock in air (Fig. 2) shows that the loss of mass in the temperature range 250–560°C is 8.4 wt %. Apparently, the loss of mass is due to the decomposition of the polymeric binder, with mostly thermal destruction characterized by low heat releases probably occurring in the initial stage of decomposition and oxidative processes starting to dominate at elevated temperatures. The maximum exothermic effect at 560°C supposedly corresponds to deep oxidation of pyrocarbon.

The insignificant loss of mass at 100–120°C corresponds to the removal of free water, which is accompanied by a weak endothermic effect.

In the temperature range above 847°C, an exothermic effect peaked at 918°C is observed, not accompanied by a change in mass, which is accounted for by the crystallization of the mineral-wool fiber.

As demonstrated by the differential loss-of-mass curves (Fig. 3), the process of thermal destruction occurs in an oxidizing atmosphere in two temperature ranges. In the first of these (up to temperatures of approximately 400°C), there mostly occur reactions not accompanied by exothermic effects. Oxidation processes occur at

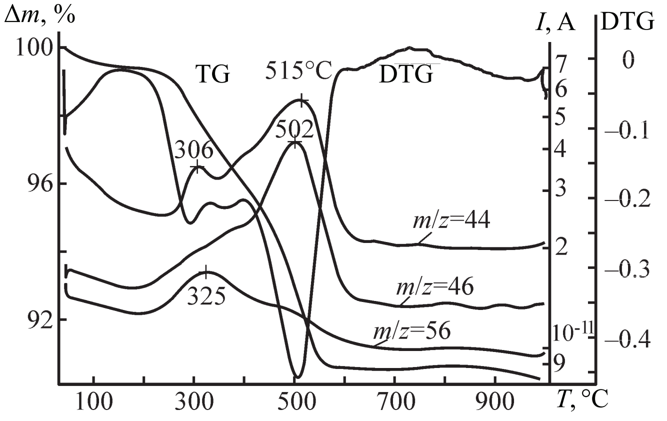

Fig. 3. Results furnished by a thermogravimetric analysis and differential thermogravimetry DTG of a mineral-wool sample in air, combined with the mass-spectrometric currents of the substances with m/z = 44, 46, and 56. (Δ*m*) Loss of mass, (*I*) current, and (*T*) temperature; the same for Fig. 4.

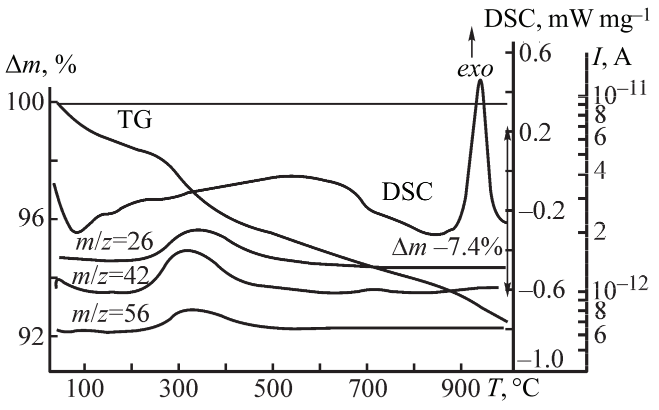

Fig. 4. Results furnished by a thermogravimetric analysis and differential scanning calorimetry DSC of a mineral-wool sample in the atmosphere of argon, combined with the mass-spectrometric currents of the substances with m/z = 26, 42, and 56.

temperatures higher than 400°C. Indeed, the peak with a mass of 44 in the mass spectrum, which corresponds to carbon(IV) oxide, i.e., to a deep oxidation with the maximum thermal effect at 502°C, nearly coincides with the peak in the differential scanning calorimetric curve at 506°C.

The assumption that the types of thermal destructions are different in different temperature ranges disagrees with the two peaks in the $m/z = 44$ mass spectrum. However, this contradiction is eliminated on the assumption that not only carbon(IV) dioxide corresponds to the ionic current at $m/z = 44$, but also such compounds as acetaldehyde, which can be formed in partial oxidation, and also propane formed in nonoxidative pyrolysis.

Indeed, an analysis of the mass spectra in the low- and high-temperature ranges revealed two groups of compounds corresponding to these temperature ranges. For example, oxygen-free hydrocarbons are released at temperatures of up to 400°C, of which acetylene (m/z = 26), propene (m/z = 42), and butene (m/z = 56) were identified. At higher temperatures, oxygen-containing compounds: ethanol (m/z = 46), propanol (m/z = 60), and butanal (m/z = 72), are identified in effluent gases. Figure 3 shows as an example the dependences of the ionic currents at m/z = 46 and 56, which corresponds to formation of ethanol and butene.

The ionic currents observed at other values of m/z = cannot be identified as individual compounds and commonly form two peaks each, one of which lies in the low-temperature range, and the other, in the high-temperature range. For example the ionic current at m/z = 30 may correspond to both ethane and formaldehyde. The curve does show two peaks.

To verify the assumption that oxygen-containing compounds are formed at temperatures higher than 400°C, we made a synchronous thermogravimetric analysis in argon. The results of this experiment are presented in Fig. 4. In this case, the mass decreases without clearly pronounced discontinuities, with the loss of mass in the temperature range under study being 7.4 wt %. If we compare this value with the change in mass upon heating in air, it becomes apparent that no less than 1.0 wet % remains in the material as a coke residue. The exothermic effect above 850°C remains unchanged in the differential scanning calorimetric curves. This effect corresponds to crystallization of the mineral component.

Pyrolysis in an inert atmosphere yields only oxygen-free products and only below 400°C. Figure 4 presents as an example, the temperature dependences of ionic currents, which correspond to acetylene (m/z = 26), propene (m/z = 42), and butene (m/z = 56).

When heated, the binder polymers undergo destruction, with backbone bonds ruptured and low-molecular gaseous and liquid volatile products formed. Despite the complex composition of the volatile products, their formation can be understood in terms of the rupture of backbone bonds, with the resulting active spe-

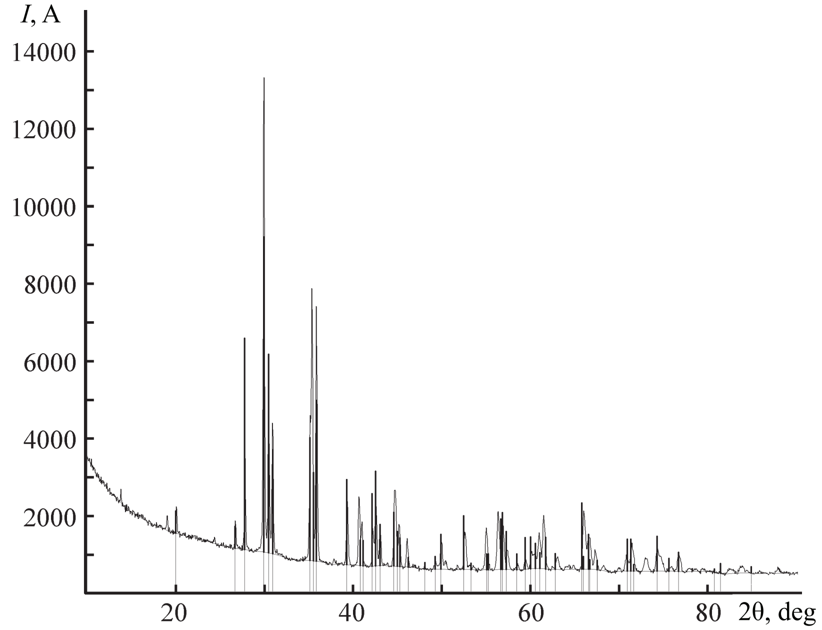

Fig. 5. X-ray diffraction pattern of a mineral-wool sample treated at 1000°C, combined with the standard X-ray diffraction pattern of augite $Ca(Mg,Fe,Al)[(Si,Al_2O]_6$. (*I*) Intensity and (2θ) Bragg angle.

cies involved in the chain transfer. The radical-chain mechanism of the main reactions in pyrolysis has been described previously [4].

With increasing temperature, the composition of the products being formed becomes more complex because the decomposition mechanism is complicated by the involvement of fillers and atmospheric oxygen in the process [5].

Thus, the thermal treatment of industrial mineral-wool articles results, beginning at 250°C in the formation of a wide variety of pyrolysis products both in an inert atmosphere and in air.

In this case, the disintegration of the mineral-wool material begins with the pyrolysis of the organic binder. As already noted, further heating of the material at higher temperatures above 850°C) is accompanied by an exothermic effect, which may be due to the crystallization of amorphous aluminosilicate. This assumption is confirmed by the results of the X-ray phase analysis.

Indeed, the starting sample is X-ray amorphous, whereas that subjected to a thermal treatment in air at 1000°C has a crystalline lattice, which corresponds to augite aluminian $Ca(Mg,Fe,Al)[(Si,Al)_2O]_6$, a mineral belonging to the group pyroxenes (Fig. 5). Under natural conditions, augite is formed by crystallization from magmatic melts as a rock-forming mineral of numerous eruptive rocks, which confirms in our case the nature of the starting fiber produced from gabbro-basalt rock.

In this case, the thermogravimetric and X-ray phase analyses of mineral-wool articles produced from slags could reveal any significant differences neither in the content of the polymer binder, nor in the nature of the phase crystallizing at high temperatures (augite).

CONCLUSIONS

(1) The study of the thermal stability of mineral-wool heat-insulating materials demonstrated that mineral-wool articles cannot be used for heat insulation of apparatus and constructions at working temperatures higher than 240–250°C. The presence of a considerable amount of organic binders in mineral-wool articles requires that adequate constructional-technological solutions should be developed to provide fire-safety of the articles used.

(2) Two temperature ranges can be distinguished in pyrolysis of the polymer binder in an oxidizing atmosphere: below 400°C, when mostly oxygen-free products are released, and above this temperature, when predominantly oxygen-containing products are released.

(3) A thermal treatment of mineral-wool articles at temperatures higher than 850°C leads to crystallization and formation of mostly the augite phase.

ACKNOWLEDGMENTS

The study was supported by the Government of Perm krai (grant under the project "Development of safe heat-insulating materials"). International research teams were financed in accordance with the Executive order of the Government of Perm krai no. 166-p of 06.04.2011.

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