Conference materials
UDC 536.46
DOI: https://doi.org/10.18721/JPM.173.202

Chemical activity of dispersed particles of potassium compounds in a pyrotechnic flame

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Abstract. Modern developments of aerosol-generating compounds are associated with increased fire extinguishing efficiency and decreased temperature and chemical activity of two-phase combustion product flow. When burning these compounds in special generators, it is important to release particles as small as possible into the environment. The concentration of these particles must be commensurate with the concentration of active flame particles in the combustible material being extinguished. The structure of particles in pyrotechnic flames has been studied and the possibility of producing particles with reduced corrosion resistance has been demonstrated. A mechanism for the interaction between reacting particles and potassium iodide crystals has also been proposed.

Keywords: flame, dispersed particle, potassium oxide, potassium iodide

Citation: Lepaev A.N., Ksenofontov S.I., Vasilyeva O.V., Tashkova K.Yu., Chemical activity of dispersed particles of potassium compounds in a pyrotechnic flame, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 17 (3.2) (2024) 14–19. DOI: https://doi.org/10.18721/JPM.173.202

Материалы конференции
УДК 536.46
DOI: https://doi.org/10.18721/JPM.173.202

Химическая активность дисперсных частиц соединений калия в пламени пиротехнического состава

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Аннотация. Современные разработки аэрозолеобразующих составов связаны с повышением эффективности пожаротушения, с понижением температуры и химической активности двухфазного потока продуктов сгорания. При горении аэрозолеобразующих составов в специальных генераторах в окружающую среду должны выбрасываться частицы как можно малых размеров. Концентрация дисперсных частиц тушащего состава должна быть соизмеримой с концентрацией активных частиц в пламени горючего вещества, подвергаемого тушению. Изучена структура дисперсных частиц в пламени пиротехнического состава. Показана возможность получения дисперсных частиц целевого продукта с уменьшенной коррозионной способностью. Предложен механизм взаимодействия реагирующих дисперсных частиц с кристаллом йодида калия.

Ключевые слова: пламя, дисперсная частица, оксид калия, йодид калия

Ссылка при цитировании: Лепаев А.Н., Ксенофонтов С.И., Васильева О.В., Ташкова К.Ю. Химическая активность дисперсных частиц соединений калия в пламени пиротехнического состава // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2024. Т. 17. № 3.2. С. 14–19. DOI: https://doi.org/10.18721/JPM.173.202

Introduction

Traditional fire extinguishing agents have several drawbacks that prevent them from being used in industrial facilities and chemical plants. Existing fire suppression systems, such as water, foam, powder, refrigeration, are characterized by high energy and material consumption. Therefore, the challenge of developing fire extinguishing devices based on aerosol-forming compounds for volume fire suppression in industrial, residential, and transportation facilities to replace current energy-intensive and costly fire suppression systems is urgent [1, 2].

During the study, pyrotechnic compositions based on nitrates, chlorates, and perchlorates of alkaline and alkaline earth metals, as well as various organic compounds, were found to have the highest fire extinguishing ability. These compounds, when burned, form an aerosol consisting of inert gases and ultradispersed and nanodispersed solid particles of chemically active compounds with a highly developed surface area. The fire extinguishing effect of these formulations is based on the inhibitory, phlegmatizing, cooling, and oxygen-binding mechanisms of action [3, 4]. For example, compositions such as C_3H_5O (20%) + $KClO_4$ (80%), C_3H_5O (20%) + $KClO_4$ (50%) + KNO_3 (30%) have been identified. The condensed phase of the aerosol consists mainly of oxide, hydroxide, and potassium salt particles ranging in size from 0.5 to 4 μm. These particles are chemically aggressive and cause corrosion of metal surfaces.

Satisfactory results were achieved with formulations containing potassium nitrate, sorbitol and ammonium iodide. The combustion products formed potassium iodide particles, which have minimal corrosive effects on protected objects. Currently, there is no literature available on the dispersed composition, morphology and elemental composition of these particles.

Materials and Methods

Two formulations based on sorbitol, potassium nitrate, ammonium iodide and iditol, potassium nitrate, dicyandiamide (DCDA) were studied in the work. The components were thoroughly mixed and pressed into a cardboard shell with a diameter of 20 mm at a specific pressure of 1000 kg/cm^2. Combustion of the composition was carried out at room conditions. Condensed dispersed particles were collected by passing glass plates through the flame.

Microphotographs of sampler areas were obtained, and the elemental composition of dispersed particles was studied using a Hitachi TM−4000Plus scanning electron microscope. In the flame, aerosol particles are formed, consisting of irregularly shaped hydrocarbon fuel residues (1), potassium carbonate (2) and potassium iodide (3). Potassium iodide is not present as an independent substance in the original pyrotechnic composition. The nucleation and growth of potassium iodide crystals to micron sizes is a new phenomenon.

Results and Discussion

The surface of the sampler is strewn with submicron-sized particles (Fig. 1, *a*). A large particle of potassium iodide (3) is presented in the form of a cube-shaped particle with an edge of 22 microns. On one of the ribs there is a particle of unburned hydrocarbon fuel (1). The sizes of the initial particles of the composition components are about 70 microns (sieve screening).

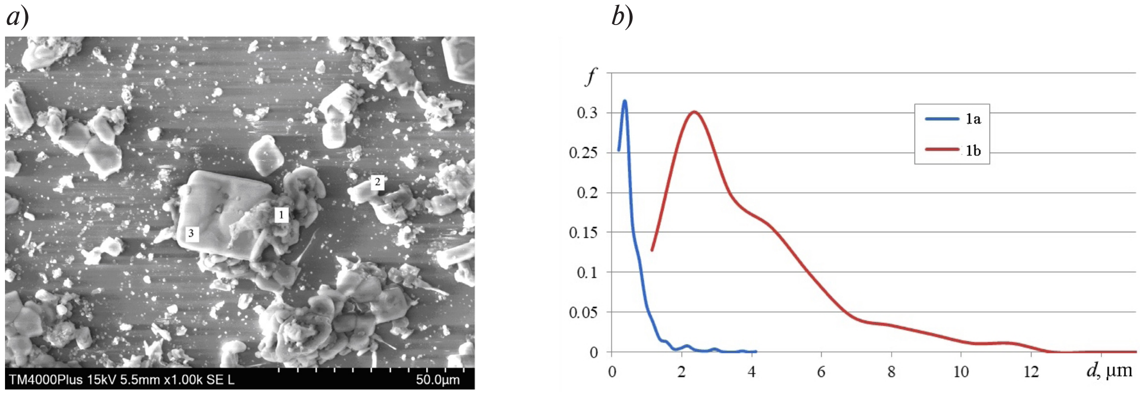

Fig. 1. Microphotograph of sampler section in SE mode of reflected electrons (*a*), particle size distribution (*b*)

The chemical composition of dispersed particles differs from each other. Separately selected areas (Fig. 1, *a*) of the sample were studied by X-ray spectral analysis, which makes it possible to judge the elemental structure of the substance under study (Fig. 2). The distribution of carbon, potassium and iodine is discrete and coincides with the contours of the particles. The coincidence of contours in the element distribution maps suggests that in the studied samples the substance can be presented in the form of K_2CO_3.

The particle size distribution function was determined using software [5]. Dispersed particles of submicron sizes (Fig. 1, *b*, curve *1a*) and large particles larger than one micron in size (Fig. 1, *b*, curve *1b*) are presented in the form of separate distribution curves. The value of the distribution function of curve 2 is increased by 7 times. The surface concentration of dispersed particles on the sampler is $109 \cdot 10^3$ particles/mm^2. Measuring the rate of passage of the sampler through the flame and the flow rate of combustion products makes it possible to determine the volumetric concentration of particles in the flame equal to $1.1 \cdot 10^6$ particles/cm^3.

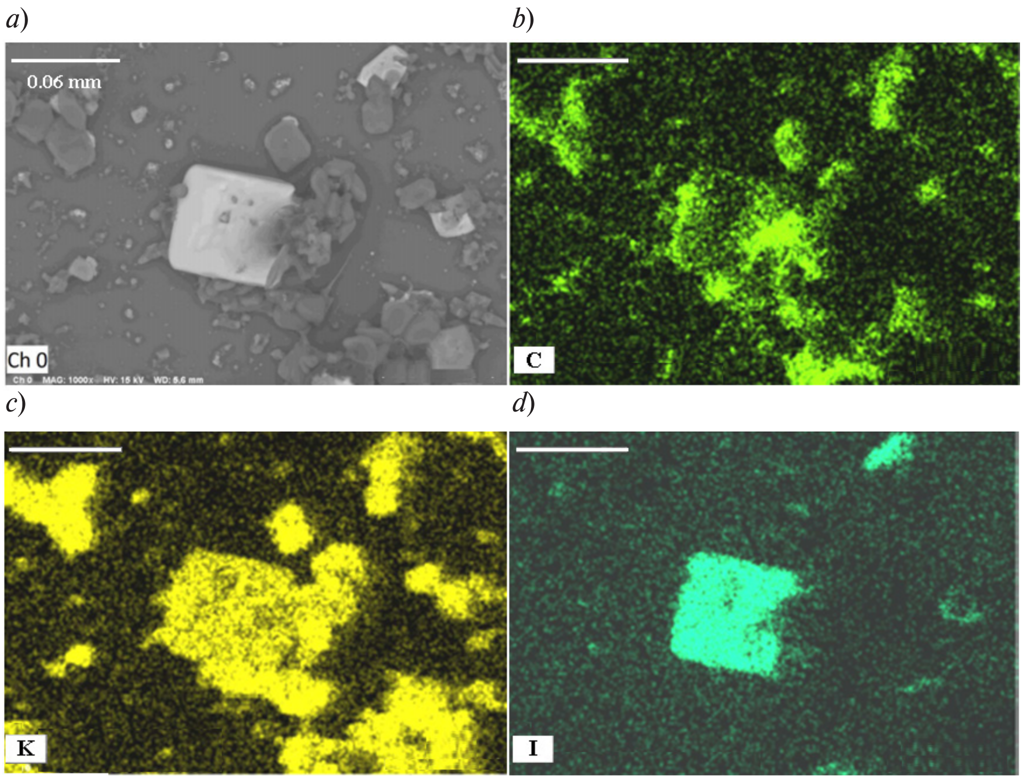

Fig. 2. Distribution maps of individual chemical elements from the analyzed area of the sample

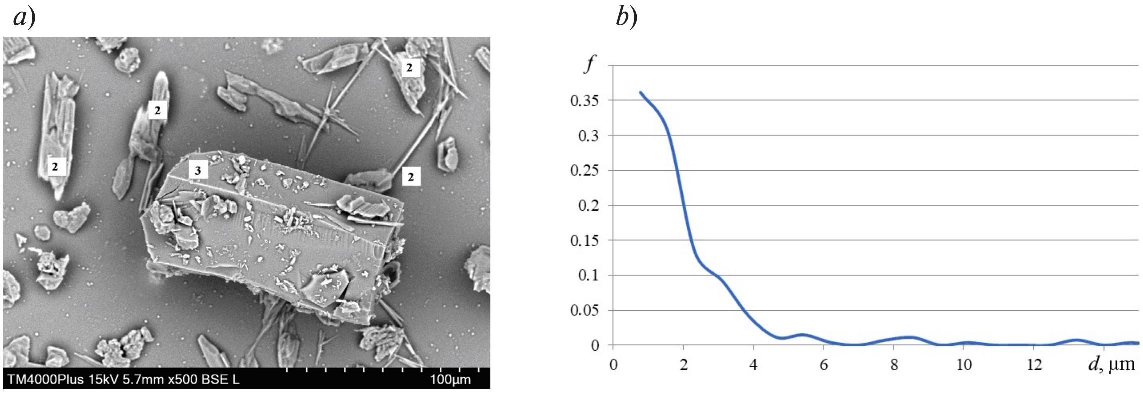

Fig. 3. Microphotograph of sampler section in SE mode
of reflected electrons (*a*), particle size distribution (*b*)

Particles found in the peripheral zone of the flame are shown in Fig. 3, *a*. A large particle of potassium iodide (3) in the shape of an irregular prism is located in the center of the picture. A lot of particles, both submicron in size and particles in the form of thin plates and elongated rods, settled on the outer surface of the prism. The concentration of submicron particles on the surface of the sampler around the prism is almost zero. The particle size distribution is shown in Fig. 3, *b*. The maximum of the distribution function occurs on a particle with a size of 0.8 μm. The average surface density of particles on the prism is $6.3 \cdot 10^3$ particles/mm^2. Analysis of Fig. 3, *a* suggests that the surface of the potassium iodide particle serves as a "third particle" for the recombination of both active flame particles – ions and electrons, and dispersed reacting particles.

It is also characteristic that "foreign" settled particles do not create defects and do not penetrate into the crystal structure. The probability of introducing "foreign" particles is not small, since the melting point of potassium iodide is 954 K, and the flame temperature measured by the photopyrometric method is 1380 K [6].

The second composition is characterized by the fact that the majority of dispersed particles consist of potassium carbonate. The observed potassium carbonate particles (2) have an irregular shape. In all likelihood, the crystallization process occurs by the surface mechanism from the liquid phase [7]. In the central zones of the flame, part of the dispersed phase consists of melt drops. Only in a narrow zone of the flame does the transition of reacting particles from the liquid phase to the crystalline phase occur. From the literature it follows that at temperatures below 693 K, potassium carbonate has a monoclinic modification, and with increasing temperature the crystal exhibits a hexagonal modification [8].

Mechanical destruction of the crystalline shell of a particle as a result of a collision with the body of the sampler leads to the appearance of whisker crystals (Fig. 4). Whisker crystals are located not only near the surface of the sampler, but are also observed in the form of bulk structures. The time of collision of dispersed particles with the surface of the sampler and the growth of whiskers is small. It is less than one millisecond. The parameters of the whiskers shown in Fig. 4 were measured using Digimazer software. The capabilities of the software allow us to estimate the size of the measured micro-object up to one nanometer. The diameter at the base of the crystals is greater than at their top. Measurements to estimate the diameter were carried out at the middle of its length $l_i = 0.5l$. The average value of the diameter of whiskers is $d = (1.4 \pm 0.5)$ μm. The average length of the crystals is $l = (25.5 \pm 3.5)$ μm. The ratio of the length of a crystal to its diameter is $l/d = 18$. This makes it possible to classify these formations as whiskers. The specific surface area of whiskers is $s/(\rho V) = 1.15 \cdot 10^3$ m^2/kg [7].

The physicochemical properties of the filamentous structures of potassium carbonate are to be studied in the future. Dispersed particles with a developed surface are used in the form of catalysts and chemical adsorbents for gaseous media. Potassium carbonate powder is used in the production of fire extinguishing agents, where the specific surface area of the fire extinguishing powder is one of the important indicators of the efficiency of stopping combustion.

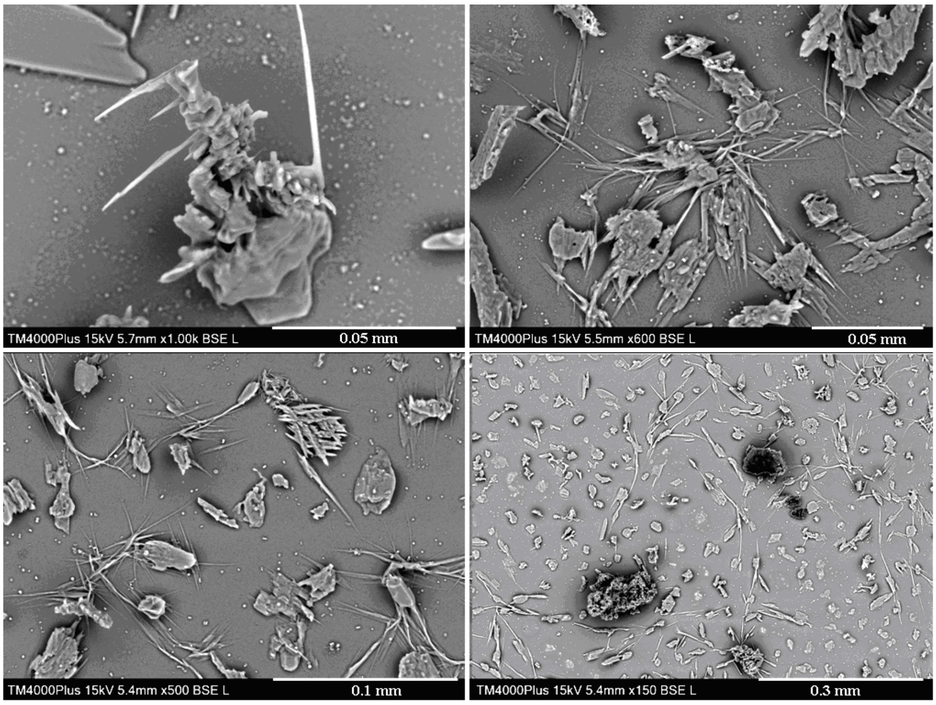

Fig. 4. Micrograph of sampler fragments

Conclusion

The substitution of potassium carbonate particles with potassium iodide particles through a chemical reaction reduces the corrosiveness of the final product.

A physical mechanism for the interaction between the reacting dispersed particles and potassium iodide crystals has been identified.

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Received 24.07.2024. Approved after reviewing 25.09.2024. Accepted 17.10.2024.