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Morphology and elemental composition of whiskers of potassium carbonate in a pyrotechnic flame

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Abstract. Pyrotechnic aerosol-forming compositions are effective fire-extinguishing agents due to the high specific surface area of the dispersed particles formed. During combustion, the initial products of the composition turn into dispersed particles in the flame zone with sharp temperature gradients. The initial products of the composition are converted into dispersed particles in the flame zone with sharp temperature gradients. The maximum particle size distribution function is 3 μm. It is not possible to obtain a similar ensemble of dispersed particles by other physico-mechanical methods. Potassium carbonate as one of the target products is formed in the form of melt particles. Crystallization of potassium carbonate starts from the outside of the melt drop and ends with the formation of crystals with a developed surface. If the integrity of the crystal shell is violated due to a collision with the body of the sampler, the melt crystallizes with the formation of whiskers. Using a scanning electron microscope, the elemental composition of crystals and filamentous structures was determined as potassium carbonate. The observed phenomenon can be recommended as a method for obtaining filamentous crystals.

Keywords: whiskers, dispersed particle, flame

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Морфология и элементный состав нитевидных кристаллов карбоната калия в пиротехническом пламени

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Аннотация. Пиротехнические аэрозолеобразующие составы являются эффективными пожаротушащими средствами из-за высокой удельной поверхности образующихся дисперсных частиц. Исходные продукты состава при горении превращаются в дисперсные частицы в зоне пламени с резкими температурными градиентами. Максимум функции распределения частиц по размерам сосредоточен при диаметре частиц 3 мкм. Другими физико-механическими способами получения аналогичного ансамбля дисперсных частиц не удается. Карбонат калия как один из целевых продуктов формируется в виде частиц расплава. Кристаллизация карбоната калия начинается с внешней стороны капли расплава и завершается образованием кристаллов с развитой поверхностью. При нарушении целостности оболочки кристалла в результате столкновения с телом пробоотборника, растекающийся расплав кристаллизуется с образованием нитевидных кристаллов. С помощью сканирующего электронного микроскопа определен элементный состав кристаллов и нитевидных структур как карбонат калия. Наблюдаемое явление может быть рекомендовано как метод получения нитевидных кристаллов.

Ключевые слова: кристаллы, дисперсная частица, пламя

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Introduction

Aerosol-forming pyrotechnic compositions are used to extinguish the fire of flammable liquids (ethanol, acetone, gasoline). Combustion products of the pyrotechnic composition consist of CO_2, CO, H_2O, N_2 gases and dispersed particles. The transformation of dispersed particles, both in terms of chemical composition and size and shape of particles, occurs as the dispersed phase moves in a two-phase flow. The target product for extinguishing a fire are dispersed particles. The concentration of such particles should be as high as possible. The dispersed particles formed in the pyrotechnic flame have minimal dimensions in diameter. Methods of mechanical grinding fail to obtain a similar fraction of dispersed particles.

The surface of dispersed particles is involved in the process of recombination of active centers in the combustion wave of a burning liquid of the form: $H^* + H^* \rightarrow H_2$. The rate of heat release in the flame is sharply reduced as a result of a decrease in the concentration of active centers. It leads to the process of extinction.

Materials and Methods

The work studied the composition based on iditol – 11%, potassium nitrate – 70%, dicyandiamide (DCDA) – 19%. 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. The combustion process was recorded using video cameras in the visible and near infrared ranges of the spectrum. The temperature distribution in the flame was determined by processing the image of the flame by the photopyrometric method. Condensed dispersed particles were collected by passing glass plates through the flame. Then the selected samples were studied by microscopy.

Photopyrometric methods make it possible to obtain the temperature distribution in the flame [1]. The temperature distribution along the height is shown in Fig. 1.

The maximum temperature is reached in the zone of bright glow of the flame and is equal to T_{max} = 1380 K. The temperature of the flame decreases with increasing height above the combustion surface, $dT/dh = -6.75$ K . mm^{-1}. The dispersed phase is formed in the flame's zone with sharp temperature gradients.

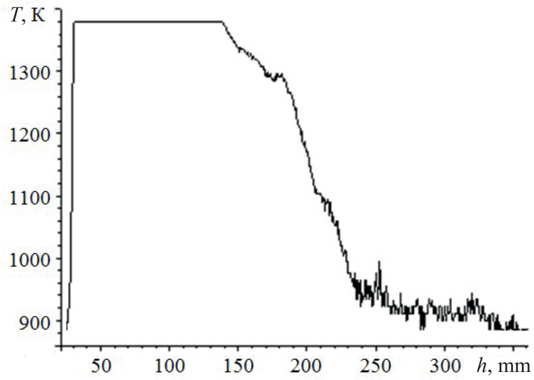

Fig. 1. The flame temperature distribution at different heights

The oxidant particles carried out by the gasification flows of the composition are shown in Fig. 2, *a*. The particle sizes of potassium nitrate at a height h = 8 mm are significant. The sizes of crystals decrease in diameter and in length (Fig. 2, *b*) with increasing height above the combustion surface (h = 14 mm). The sizes of dispersed particles also decrease in the peripheral zone (Fig. 2, *c*). Optical processing of the image of particles introduced into the computer according to the developed program was carried out [2].

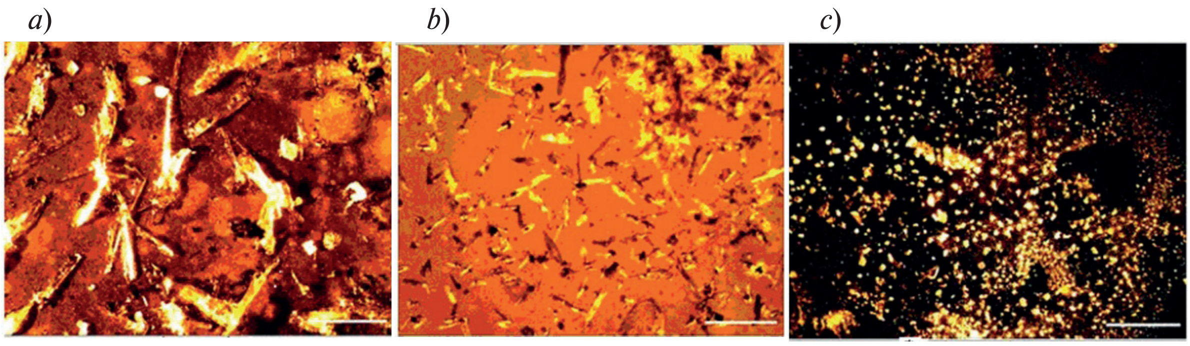

Fig. 2. Micrographs of the sampler area: h = 8 mm, central zone (*a*); h = 14 mm, central zone (*b*); h = 8 mm, peripheral zone (*c*). Benchmark 1 mm

The analysis of the ensemble of dispersed particles using software showed that the maximum particle size distribution function is 3 μm (Fig. 3). However, the resolution of the optical microscope used to study the ensemble of dispersed particles does not reflect the structure of dispersed particles.

An electron scanning microscope Hitachi TM−4000Plus was used to decipher the particle morphology and elemental composition of the sample. The condensed combustion products have

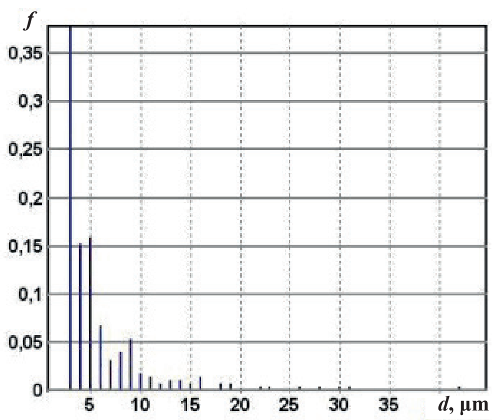

Fig. 3. Particle size distribution

a complex particle structure in shape and size. The section of the sampler in reflected electron beams is shown in Fig. 4.

The method of X-ray spectral analysis, implemented on a scanning electron microscope, showed that among the particles there are unburned particles of organic fuel. These particles contain more carbon (Fig. 5). These particles predominantly contain carbon. There are particles of potassium carbonate in the form of particles of irregular crystal structure [3, 4].

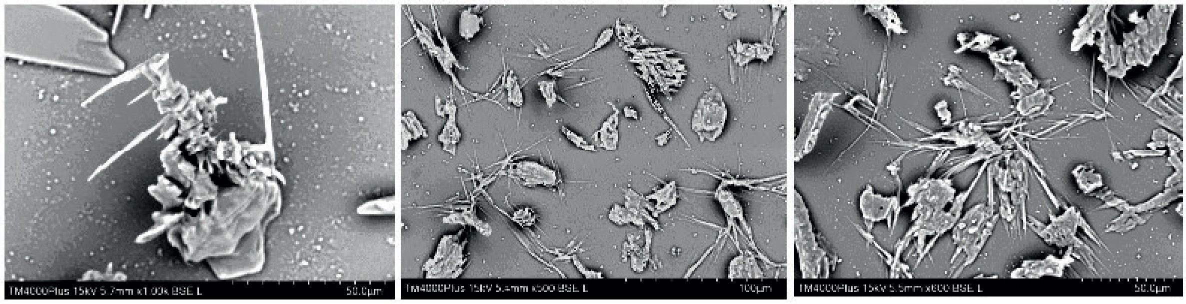

Fig. 4. Micrograph of sampler fragments

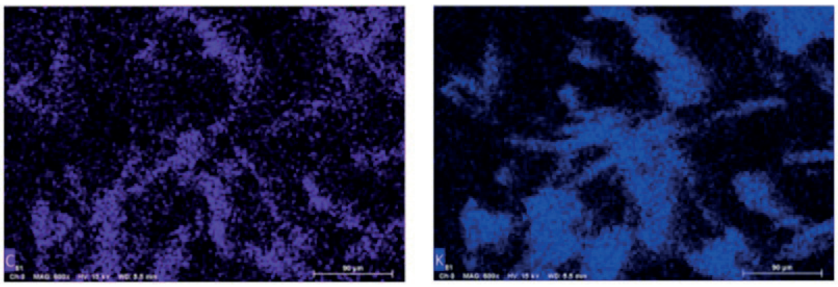

Fig. 5. Distribution map of chemical elements

Results and Discussion

The potassium carbonate formed in the flame, according to the conditions of the experiment, must be in a liquid state or decompose. The melting point of potassium carbonate is 1164 K [5]. However, irregularly shaped potassium carbonate crystals are observed on the sampler. The number of such deposited particles is quite large. Potassium carbonate crystals, according to the literature data, at low temperatures ($T < 693$ K) have a monoclinic structure. The crystal structure transforms into a hexagonal modification with increasing temperature. The presence of particles of complex shape allows us to say that the process of crystallization of the substance comes from the outer surface. There are many nuclei in the form of molecules, ions and dispersed particles for the formation of crystals in the surrounding space. For this reason, the external shape of the particles is different.

Inside the crystalline shell, the substance can be in a liquid state. After some time, the molten product passes into a crystalline state. The crystalline shell at the moment of particle collision with the surface of the sampler cannot withstand the "overload" and is forced to collapse. Liquid is "ejected" from the formed cracks and forms crystals in the form of filaments.

The detection and growth of whiskers in the flames of pyrotechnic compositions proved possible as a result of careful experimental studies. Skipping the process of crystal formation shells with a liquid phase inside it, would allow us to detect only irregularly shaped potassium carbonate crystals in the studied samples.

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 time of particle interaction with the sampler is determined by the flow rate of combustion products. This speed does not exceed 1 m/s. For the first time, the appearance of whiskers from potassium carbonate was discovered in such a short time.

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 $s/(\rho V) = 1.15 \cdot 103$ m^2/kg.

The dispersed phase has additional possibilities for the formation of new particles and an increase in the surface of particles. This is evidenced by the presence of a liquid mass in the particles of potassium carbonate. The process of formation of new structures during the collision of complex dispersed particles can be recommended as a method for obtaining whiskers.

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.

Whiskers are produced from refractory materials such as SiC, SiN, Al_2O and MgO on an industrial scale [6]. The time for growing whiskers up to 1 mm from the gas phase is several days, from the melt it is up to several minutes. Whiskers have completely new physical and chemical properties compared to single crystals, because they do not contain crystal defects.

Conclusion

1. The structure of the flame of an aerosol-forming pyrotechnic composition has been studied. The zone of formation of the dispersed phase has been identified. Here the temperature gradient has a negative value.

2. Crystallization of potassium carbonate occurs from the outside of the melt. The melt crystallizes with the formation of whiskers when the integrity of the crystal shell is broken.

REFERENCES

1. **Porfiriev A.M., Ksenofontov S.I.,** Programma opredeleniya polya temperatur plamen “Flame – temperature”, Nauka i obrazovanie. 8 (2010) URL: http://ofernio.ru/portal/newspaper/ofernio/2010/8.doc.

2. **Porfiriev A.M., Ksenofontov S.I.,** Chastica, Nauka i obrazovanie. 6 (2010) URL: http://ofernio.ru/portal/newspaper/ofernio/2010/6.doc.

3. **Tashkova K.Yu., Ugolkova A.S., Ksenofontov S.I., Vasilyeva O.V.,** Morfologiya i himicheskij sostav chastic pirotekhnicheskogo aerozolya dlya obemnogo pozharotusheniya, Sb. mat. XVII Mezhdunarod. nauch.-prakt. konf. “Rossijskaya nauka v sovremennom mire”, MSU, Moscow. (2018) 129–132.

4. **Tashkova K.Yu., Guryanov A.A., Lepaev A.N., Ksenofontov S.I., Vasilyeva O.V.,** Himicheskaya aktivnost aerozolya pirotekhnicheskogo sostava obemnogo pozharotusheniya, Sb. mat. VII Vseros. konf. s mezhdunar. uchastiem “Aktualnye voprosy himicheskoj tekhnologii i zashchity okruzhayushchej sredy”, ChSU, Cheboksary. (2018) 45–46.

5. **Grigoriev I.S., Meilikhov E.Z.,** Fizicheskie velichiny. Spravochnik, Energoatomizdat, Moscow, 1991.

6. **Artemyev S.R.,** Svojstva i osnovnye sposoby polucheniya nitevidnyh kristallov, Vostochno-Evropejskij zhurnal peredovyh tekhnologij. 5/1 (65) (2013) 22–25.

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