Researches of ice-forming efficiency of products of sublimation of pyrotechnic compositions consisting of silver iodide agi particles and zinc oxide nanotubes

B M Khuchunaev, Kh- M Kh Baysiev, S O Gekkieva*, A Kh Budaev

Federal State Budgetary Institution «High-Mountain Geophysical Institute», 2 Lenina avenue, Nalchik, 360030, The Russian Federation

E-mail: gekkieva@list.ru

Abstract. The article is a continuation of experimental research on the search for new, more effective compositions for active effects on clouds and fogs. The paper also presents the results of studies of the ice-forming efficiency of pyrotechnic compositions based on AgI and zinc oxide nanotubes. The dependence of the specific yield of ice-forming active particles for various zinc contents in the initial composition of AD-1 was revealed.

1. Introduction

Over the past decades, in many countries a huge number of theoretical, laboratory and field studies have been carried out on the means of influencing clouds and precipitation, answers to many questions have been received, and valuable diverse experimental material has been collected. However, the issue of developing new and improving existing compositions remains relevant today. AgI iodide silver pyrotechnic compositions are one of the most widely used reagents for active effects on clouds. It is believed that the crystal structure of AgI is similar to the structure of natural ice; therefore, it is an effective reagent for influencing supercooled cloud systems. The formation of the ice phase on AgI aerosol particles has been studied by many researchers. In early works [1, 2], it was assumed that ice crystals formed on AgI aerosol particles due to sublimation of water vapor upon saturation relative to ice. However, the development of condensed matter physics in recent years shows that the growth of a new phase on catalyst particles, such as the growth of ice on reagent particles, is a more complex process.

This paper presents the results of experimental studies on ways to increase the ice-forming efficiency of crystallizing reagents of anti-hail products. The main goal of the research was to determine the effect on the yield of ice-forming particles of various chemical components that increase the yield of ice-forming particles from one gram of reagent. As such a component, finely dispersed zinc powder was used in the experiments, with particle sizes from 0.01–0.05 mm, which were introduced into the initial pyrotechnic composition of AD-1 in relation to its total mass — 3%, 6%, and 9%, respectively. Zinc has a crystal lattice closer to the ice crystal lattice [3]. The pyrotechnic composition of AD-1 in relation to its total mass is 3%, 6%, and 9%, respectively.
2. Methods and materials

Structural and physical characteristics of zinc

Zinc crystals have a hexagonal packing of atoms, which are very similar to the structure of ice. Zinc is a brittle transition metal of a bluish-white color, which oxidizes in air, being covered with a thin layer of zinc oxide. It has a low melting point. At 100-150 °C, zinc is plastic, at a temperature of 419 °C it begins to melt, but if the boiling point is 913 °C, it begins to turn into steam. It was shown in [4–6] that upon sublimation of zinc in the presence of graphite, zinc oxide nanotubes are formed. The formation of nanotubes occurs according to the well-known drip mechanism. The physical essence of the droplet mechanism lies in the fact that the formation of a closed interface of three phases adjacent to the singular face of the crystallization front, and the creation of conditions under which a drop of capillary pressure arises in the droplet or an uncompensated surface tension applied to the wetting perimeter provides a shift of the phase boundary in the direction of crystal growth. The role of the phase boundaries during the growth of whisker nanocrystals by the aforementioned dropping mechanism is to reduce the crystallization barriers due to the release (discharge) of a spheroidizing drop of excess free energy and lowering the saturation necessary for the growth of the singular vertex face of the nanowire at a given speed, as well as to ensure that the specified face steady equilibrium drops. The driving force of the process of moving the droplet is the excess of free energy, the source of which is the outer surface of the droplet. The crystallizing substance diffuses into this drop, precipitates at the liquid – crystal interface, and the drop remains on top. The growth rate under the drop is one to two orders of magnitude higher than other growth mechanisms.

In our experiments, at a high combustion temperature of the pyrotechnic composition of anti-hail products, zinc oxide nanotubes are also formed, in this case the catalyst (graphite) is part of AD-1.

The equipment and methodology for the experiment

Figure 1 shows a set of equipment for studying the ice-forming properties of reagents. To carry out the full cycle of the experiment, it is required: a 1m³ sublimation chamber, a 9m³ large cloud chamber, a 0.080 m³ small cloud chamber, a device for creating a cloud environment, an Adventurer electronic balance, a reagent atomization device, a reagent sublimation device at high pressures, a microscope Motic for counting the number of crystals. In a large cloud chamber, the temperature can be maintained from 0 ° to –17 °C, in a small cloud from 0 ° to –25 °C [4-6].

![Figure 1. A Set of equipment for studying the ice-forming properties of reagents](image)

3. Results

Laboratory experiments to determine the specific yield of ice-forming particles using AD-1 reagent with zinc nanotubes were carried out with different weight fractions (3, 6, 9% of the weight of AD-1). The determination of the yield of crystallization nuclei for each sample is calculated according to the generally accepted method [4-6].
Figure 2 shows the crystals deposited on the substrate, which were formed upon the introduction of pyrotechnic composition AD-1 and AD-1 with zinc additives.

![Crystals deposited on the substrate](image)

Figure 2. Ice crystals on a substrate when AD-1 and AD1 + zinc reagent is introduced into the cloud chamber: a - ice crystals when adding AD-1, b - ice crystals when adding AD-1 + zinc (3%), c - ice crystals when adding AD1 + zinc (6%), d - ice crystals when adding AD1 + zinc (9 %)

Table 1 presents the experimental data of the component of the reagent AD-1 without additives at temperatures from -5.9 °C to -10.2 °C.

Table 1. Average results of crystallization nuclei of pyrotechnic composition AD-1 with zinc additives at various temperatures

| Temperature, °C | Mass of reagent AD-1, g | Specific output, g⁻¹ |
|-----------------|-------------------------|-----------------------|
| -13.4           | 0.01                    | 4.4x10⁻¹²            |
| -11.9           | 0.01                    | 5.7x10⁻¹²            |
| -10.6           | 0.01                    | 1.2x10⁻¹²            |
| -10.2           | 0.01                    | 1.2x10⁻¹²            |
| -9.7            | 0.01                    | 6.4x10⁻¹²            |
| -9.5            | 0.01                    | 5.0x10⁻¹²            |
| -9.1            | 0.01                    | 6.2x10⁻¹²            |
| -8.7            | 0.01                    | 1.3x10⁻¹²            |
| -8.2            | 0.01                    | 3.3x10⁻¹²            |
In total, laboratory experiments confirm that the presence of finely dispersed zinc powder in the composition of the initial ice-forming fuel in relation to the total mass of 6% sharply increases the yield of ice-forming particles in the entire range of accepted temperatures, from zero to minus 14 °C.

| Temperature, °C | Mass of reagent AD-1+Zn(3%), g | Specific output, g⁻¹ |
|----------------|---------------------------------|----------------------|
| -12.5          | 0.01                            | 1.7x10¹³             |
| -12.3          | 0.01                            | 1.7x10¹³             |
| -11.5          | 0.01                            | 9.4x10¹²             |
| -10.5          | 0.01                            | 1.1x10¹³             |
| -9.2           | 0.01                            | 2.0x10¹³             |
| -9             | 0.01                            | 1.1x10¹³             |
| -8.7           | 0.01                            | 8.6x10¹²             |
| -8.5           | 0.01                            | 1.9x10¹³             |
| -7.5           | 0.01                            | 9.9x10¹²             |
| -5.5           | 0.01                            | 9.0x10¹²             |
| -4.4           | 0.01                            | 1.1x10¹³             |
| -2.2           | 0.01                            | 8.2x10¹²             |

| Temperature, °C | Mass of reagent AD-1+Zn(6%), g | Specific output, g⁻¹ |
|----------------|---------------------------------|----------------------|
| -13.3          | 0.01                            | 1.0x10¹⁴             |
| -12.2          | 0.01                            | 1.43x10¹⁴            |
| -10.4          | 0.01                            | 1.02x10¹⁴            |
| -10            | 0.01                            | 6.0x10¹³             |
| -9.6           | 0.01                            | 5.2x10¹³             |
| -7.5           | 0.01                            | 5.4x10¹³             |
| -5             | 0.00052                         | 1.8x10¹³             |
| -4.2           | 0.00052                         | 1.2x10¹³             |
| -3.4           | 0.00052                         | 1.0x10¹³             |
| -2.2           | 0.00052                         | 1.3x10¹³             |
| -1.6           | 0.00052                         | 4.7x10¹²             |
| -1             | 0.00052                         | 6.6x10¹²             |

| Temperature, °C | Mass of reagent AD-1+Zn(9%), g | Specific output, g⁻¹ |
|----------------|---------------------------------|----------------------|
| -12.7          | 0.01                            | 3.5x10¹³             |
| -12.1          | 0.01                            | 3.2x10¹³             |
| -11.3          | 0.01                            | 1.9x10¹³             |
| -10.7          | 0.01                            | 1.4x10¹³             |
| -10            | 0.01                            | 2.1x10¹³             |
| -9.5           | 0.01                            | 1.6x10¹³             |
| -7.2           | 0.01                            | 1.3x10¹³             |
| -7             | 0.01                            | 7.2x10¹²             |
| -5.9           | 0.01                            | 1.3x10¹³             |
| -5.2           | 0.01                            | 5.1x10¹²             |
| -4.5           | 0.01                            | 3.9x10¹²             |
| -4.3           | 0.01                            | 6.2x10¹²             |
With the addition of 9% zinc, there is a decrease in the specific yield of ice-forming particles. The physics of such a decline is still difficult to explain.

In figure 3 shows the dependence of the yield of ice-forming active particles (n) for various contents of finely divided zinc powder in the initial composition of AD-1. Curve 1 characterizes the yield of ice-forming particles from one gram of the initial AD-1 composition without zinc in it, curve 2 with a zinc content of 3%, curve 3 with a zinc content of 9% and curve 4— with a zinc content of 6%.

![Figure 3. Output of active particles (n) for different concentration of dispersed zinc powder in AD-1 compound](image)

The results of experiments conducted with various mass concentrations of zinc in the range from 0 to 9% are presented in table 2.

**Table 2.** The specific yield of active particles of the reagent AD-1 with the addition of zinc

| t, °C | C_{Zn}, % | -11 Specific output, g⁻¹ | -9 Specific output, g⁻¹ | -7 Specific output, g⁻¹ | -5 Specific output, g⁻¹ |
|------|-----------|---------------------------|-------------------------|-------------------------|-------------------------|
| 0    |           | 3.2×10^{12}               | 2.7×10^{12}             | 2.5×10^{12}             | 6.5×10^{11}             |
| 1    |           | 8.8×10^{12}               | 7.0×10^{12}             | 5.6×10^{12}             | 1.2×10^{12}             |
| 2    |           | 1.5×10^{13}               | 1.2×10^{13}             | 8.2×10^{12}             | 4.5×10^{12}             |
| 3    |           | 2.8×10^{13}               | 2.2×10^{13}             | 1.1×10^{13}             | 7.2×10^{12}             |
| 4    |           | 4.6×10^{13}               | 3.6×10^{13}             | 1.6×10^{13}             | 9.5×10^{12}             |
| 4.7  |           | 6.5×10^{13}               | 5.2×10^{13}             | 2.5×10^{13}             | 1.1×10^{13}             |
| 5    |           | 7.0×10^{13}               | 5.9×10^{13}             | 3.0×10^{13}             | 1.3×10^{13}             |
| 5.5  |           | 7.3×10^{13}               | 6.2×10^{13}             | 3.3×10^{13}             | 1.5×10^{13}             |
| 6    |           | 7.5×10^{13}               | 6.3×10^{13}             | 3.4×10^{13}             | 1.6×10^{13}             |
| 6.6  |           | 6.5×10^{13}               | 5.2×10^{13}             | 2.5×10^{13}             | 1.4×10^{13}             |
| 7    |           | 5.2×10^{13}               | 4.3×10^{13}             | 1.9×10^{13}             | 1.0×10^{13}             |
The specific yield of active reagent particles depending on the concentration of powdered zinc is shown in figure 4. From the presented graph it is seen that the maximum yield of active ice-forming particles is provided in the range of zinc concentrations of 4.7-6.6 mass. %. This area in Fig. 4 is limited by vertical lines. From the above materials it follows that the presence of finely dispersed zinc powder in the initial ice-forming fuel in the ratio to the total mass of 6% sharply increases the yield of ice-forming particles in the entire range of accepted temperatures, from zero to minus 14 °C. This increase in the yield of active ice-forming particles in the temperature range under study is explained by the fact that zinc oxide nanotubes of various modifications and sizes that actively interact with a supercooled cloud medium in the accepted temperature range are formed at a high combustion temperature of the pyrotechnic composition. So, for example, at a temperature of minus 12 °C (curve 3 on the graph), the yield of ice-forming particles increases by almost an order of magnitude, and in the temperature range from minus from 2 °C to minus 4 °C - almost doubles, which makes it possible to affect warmer supercooled part of the cloud.

![Figure 4. Dependence of specific output of ice-forming particles from zinc concentration in pyrotechnical compound AD-1 for different temperatures](image)

**Summary**

1. The work presents the results of original studies, which showed that the presence of finely dispersed zinc powder in the composition of the initial ice-forming fuel AD-1 in relation to the total mass of 6% sharply increases the yield of ice-forming particles over the entire range of accepted temperatures.
2. The specific yield of ice-forming particles at a temperature of minus 12 °C increases almost by an order of magnitude, and in the temperature range from minus 2 °C to minus 4 °C - twice.
3. Based on the initial ice-forming fuel AD-1, a methodology has been developed for obtaining an effective pyrotechnic composition for equipping meteorological rockets designed for active impact.
on thundercloud clouds with the aim of artificially increasing liquid precipitation and combating hail.

4. This composition can also be used to create promising ground-based generators for active impacts on supercooled mists, in order to provide favorable meteorological conditions for the functioning of spaceports, airports and road transport communications.

References

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