THE STUDY OF HIGH EFFICIENT AgI PYROTECHNICS AND THEIR NUCLEATING PROPERTIES*

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ABSTRACT

Two kinds of high efficient AgI pyrotechnics BR−88−5 and BR−91−Y have been developed. The tests in the cloud chamber show that the AgI ice nucleating effectiveness can reach up to 10^{15}/g, and the BR−91−Y has even higher ice nucleating rate. Two kinds of foreign AgI pyrotechnics have been made according to the given formulations and also tested in the cloud chamber for comparison. X−ray diffraction analysis for the aerosols produced by burning BR−91−Y shows that AgI in aerosols still retains the hexagonal crystal form and the lattice parameters are smaller than those of pure AgI and other AgI composite nuclei, and closer to ice. Combining with the other tests, the reasons for the high efficiency of BR−91−Y have been discussed.

Key words: artificial ice nuclei, AgI−pyrotechnic, ice nucleating properties, lattice parameters of AgI

I. INTRODUCTION

β−AgI has the hexagonal crystal structure and its lattice parameters are very close to ice. The fine particles of AgI can act as ice nuclei through heterogeneous nucleation to produce ice crystals in supercooled clouds and the ice nucleating threshold temperature is about −4°C, which is the best artificial ice nuclei that have been found so far. In the application of weather modification, burning AgI−acetone solutions or pyrotechnics are usually used to generate ice nucleus aerosols. AgI pyrotechnics have the advantage of adaptable to varied carrying tools for cloud seeding. Many kinds of pyrotechnics have been made in other countries. They generally consist of AgI, oxidant, combustible, binder and other additives. Their compositions are quite different and the AgI aerosols generated by them vary in their ice nucleating properties.

Previous researches have shown that the nucleating capability of ice nuclei in heterogeneous nucleation depends on the extent to which it changes the orientation of the adsorbed water molecules and forms the ice−like structure. The less differences of lattice parameters between ice and nucleus particles, the less interfacial strain and lower energy barrier during the epitaxial growth of ice (Turnbull and Vonnegut 1952). The lattice parameters of AgI are already close to ice; if the lattice misfit with ice could be reduced, the ability of nucleation would be further

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improved. Much efforts have been paid for this purpose to develop AgI composite nuclei. Vonnegut and Chessin (1971), Passarelli et al. (1973; 1974), and Palanisamy et al. (1986) made AgI–AgBr, AgI–CuI and AgI–AgCl solid solutions or composite aerosols in laboratories, respectively. X–ray analyses showed that they had the face–centered cubic crystal structure and the (111) plane of the crystal is similar to the (0001) plane of ice. Their lattice parameters could change with the mole ratio of added compound and the misfit with ice reaches a minimum under a certain mole ratio. Their ice nucleation capability and threshold temperature are obviously increased. The added impurity would create hydrophilic center or structure imperfections and increase the active site on surface. It might be another reason for improvement of the nucleating capability. Recently, Scott et al. (1989) produced an ice nucleant aerosol by combustion of a 2% AgI–0.5 mole % BiI_3–NH_4I–acetone–water solution. The aerosol was identified as the hexagonal crystal form with close match to ice, and the ice nucleating effectiveness of this aerosol is an order of magnitude greater than AgI alone at $-10^{\circ}C$.

On the other hand, the nucleation mechanism of AgI–containing aerosol particles can be changed with the attached chemical composition. The aerosol particles of pure AgI and AgI–AgCl solid solution are hydrophobic and they produce ice crystals in clouds mainly through contact nucleation mechanism with a very slow nucleating rate (DeMott et al. 1983). Some AgI–containing aerosols such as AgI–NaI, (Blumenstein et al. 1983), AgI • AgCl–NaCl (Feng and Finnegan 1989) and the aerosol generated by Russian Silverspare pyrotechnic (Federer and Schneider 1981) are through condensation–freezing nucleation mechanism with a high nucleating rate, owing to the aerosol containing hydrophilic compositions.

The research about AgI composite ice nuclei is significant for weather modification. Some composite ice nucleus aerosols generated by acetone solution combustion system begin to be used in field operations. However, the results of these researches were scarcely applied in making AgI pyrotechnics; the only report from Huter et al. (1988) showed that their VTG–8B AgI pyrotechnic containing CuI raised the effectiveness at higher temperature. In fact, AgI pyrotechnic has more chemical compounds taking part in the combustion process and more easy to produce AgI composite ice nuclei. The problem is to develop a good formulation.

Referring to the formulations of foreign pyrotechnics and introducing the research results of AgI composite nuclei, in the present work for developing the high efficient AgI pyrotechnic we reduced the amount of AgI, adding in iodide–rich compound and copper salt.

II. EXPERIMENTAL PROCEDURES

There is no standard instrument or equipment for the ice nucleus measurement. The ice nucleating properties of the aerosol produced by pyrotechnic are found out mainly through the tests in cloud chambers. The general opinion is that the cloud chamber with volume of several cubic meters is easier to be controlled and the test result is rather reliable. In this work all tests were carried out in a 2 m^3 isothermal cloud chamber (Feng et al. 1990). The cloud chamber is first cooled to a required temperature and the cloud produced by ultrasonic nebulizer is sent to the chamber to remove the background ice nuclei; then the flow of sending cloud is adjusted to keep the liquid water content around 1.5—2.0 g/m^3 at the beginning of each run. A small pyrotechnic column (2.5—3 g) is burned at the lower entrance of a vertical dilution wind tunnel and the produced aerosol is diluted by mixing up with the surrounding air in the tunnel, then extracted by a syringe at the center of the tunnel. All or part of the aerosol in the syringe is injected to the chamber to be tested. The ice crystals nucleated by the aerosol grow in the chamber and fall, then are caught by a pack of slides at the chamber bottom. Slides will be taken out one after another in a time interval of 1–5 minutes, then the ice crystals are observed and counted under a microscope until no crystal is observed any more. Assuming each ice nucleus nucleates ice once and the aerosol in the chamber diluted by sending cloud airflow is neglected, the nucleation effectiveness in terms of per gram AgI can be calculated as follows:

$$E = \frac{N_{ice} A_c F t}{A_v m V},$$

where E is the nucleation effectiveness in terms of per gram AgI, N_{ice} the cumulative crystal number in a view field of microscope, A_c the cross section area of the chamber, A_v the view field area of microscope, F the airflow in the dilution wind tunnel, V the volume of the aerosol sample, t and m the burning time and mass of pyrotechnic column.

The tests of ice nuclei always indicate there is large error owing to the fact that ice nucleation is sensitive to the test conditions which are not easy to be controlled. So it is hard to compare the test results from different cloud chambers. In our 2 m^3 cloud chamber temperature can deviate $\pm$ 0.15°C from the average value in a run and cause the effectiveness error of about 1.5 times. The local supersaturation in the cloud chamber can result from sending cloud even in the volume only about 0.2—0.7% of the chamber; it will cause more nuclei to be actived, accelerate the nucleating rate and raise the effectiveness to about 2—3 times. Liquid water content in the chamber usually decreases when a large number of ice crystals comes out. It will reduce the testing nucleating rate but has no influence on the effectiveness. The surrounding wind speed will affect the airflow in the wind tunnel and make $\pm$ 5% error in calculating the ejected mass of AgI. Ice crystals are underestimated about 8% by eye. Additionally, the effectiveness will be underestimated about 10% due to the airflow dilution. Altogether the test error of effectiveness is about $\pm$ 2.5 times, which is consistent with the fact that all data of effectiveness for one formulation of pyrotechnic deviate within 5 times. It indicates that the test in the 2 m^3 cloud chamber has good reproducibility with small data variances, and is satisfactory for present study.

III. FORMULATION SELECTION AND COMPARISON

The ice nucleating properties have been taken as indexes for selection and comparison of pyrotechnic formulations. All tests are conducted mainly through cloud chamber experiments.

1. *Test Results of TB–1 and Silverspare Pyrotechnics Imitation*

In order to get experience and data for comparison the TB–1 (American) and Silverspare (Russian) pyrotechnics were first made according to the given formulations (Sax et al. 1979; Federer and Scheider 1981) and tested in the cloud chamber. The effectiveness is shown in Figs. 1 and 2 respectively along with the test results of original products in the ETH 100 L cloud chamber of Switzerland and in the other chambers. It can be seen that the effectiveness tested in the 2 m^3 cloud chamber is higher than that from other chambers and with minimum deviation. It might be due to the 2 m^3 cloud chamber having larger volume and therefore longer time for the aerosol nucleation. The tests also show that Silverspare has much higher effectiveness than TB–1. Because the original samples of these two pyrotechnics could not be obtained, even with

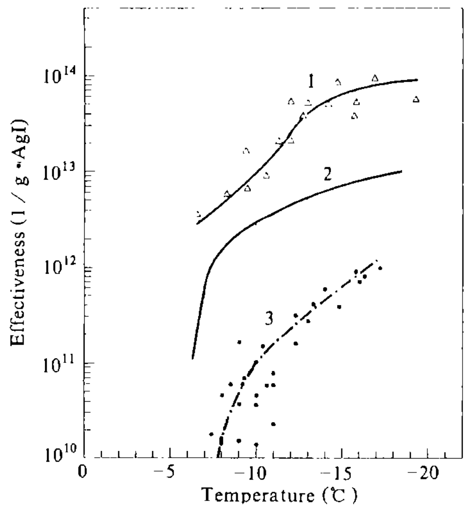

Fig. 1. Ice nucleating effectiveness of TB−1 tested by three cloud chambers. 1. 2 m^3 cloud chamber (China); 2. CSU 960 L cloud chamber (America); 3. ETH 100 L cloud chamber (Switzerland).

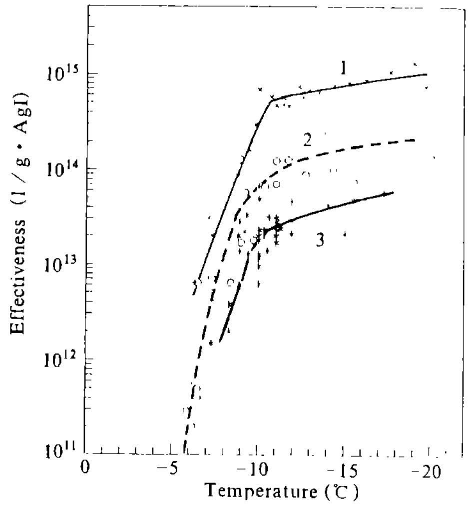

Fig. 2. Ice nucleating effectiveness of Silverspare tested by three cloud chambers. 1. 2 m^3 cloud chamber (China); 2. Cloud chamber of CAO (Russian); 3. ETH 100 L cloud chamber (Switzerland).

the same composition, they might have some differences in manufacture. However, the tests of these two pyrotechnics in the ETH 100 L cloud chamber also show that Silverspare is better than TB−1 in nucleating effectiveness. This is very useful information for developing the new pyrotechnic.

2. *Screen Test of New Pyrotechnic Formulation*

The pyrotechnic includes many chemical compounds which have comprehensive effects on ice nucleating properties. It is impossible to test each composition one by one. After drawing out a basic formulation, the experiments have been carried out concentrated on two respects. One is changing AgI ratio in the formulation (they are 0.5%, 1%, 1.2%, 1.5%, 2% and 3%). The highest effectiveness is obtained from the pyrotechnic containing 1% AgI. Another is adding different copper salt in the basic formulation. Altogether thirty odd formulations have been made and about four hundreds cloud chamber tests for ice nucleating efficiency have been conducted. Finally, the best two formulations BR−88−5 and BR−91−Y which contain organic copper salt have been obtained. A part of the screen test results are shown in Fig. 3. Curve 1 indicates the ice nucleating effectiveness of the basic formulation with 1% AgI not containing copper salt; the different symbol dots represent different copper salts, and curve 2 is the BR−91−Y formulation.

3. *Effectiveness and Comparison with Other Pyrotechnics and AgI−Acetone Solution Systems*

The ice nucleating effectiveness of BR−88−5 and BR−91−Y has been tested over a temperature range from −3.5°C to −20°C. The results are shown in Fig. 4 along with the results for TB−1 and Silverspare. It can be seen that the effectiveness of BR−91−Y and BR−88−5 can reach up to 10^{15} / g (AgI) in the temperature range from −7.5°C to −20°C about 4—40 times

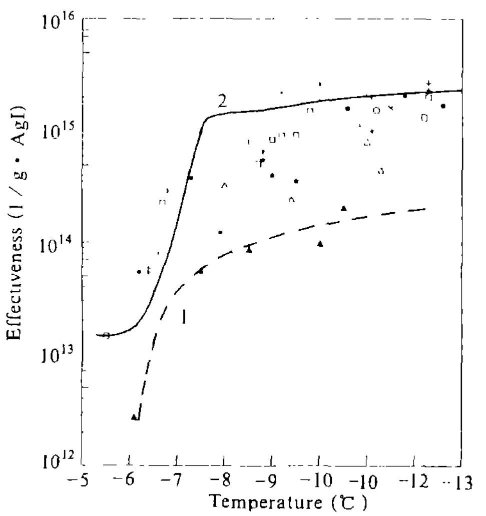

Fig. 3. Results of ice nucleating effectiveness screen tests (different symbols represent different copper salts added in). 1. Basic formulation (1% AgI) without copper salt; 2. BR–91–Y.

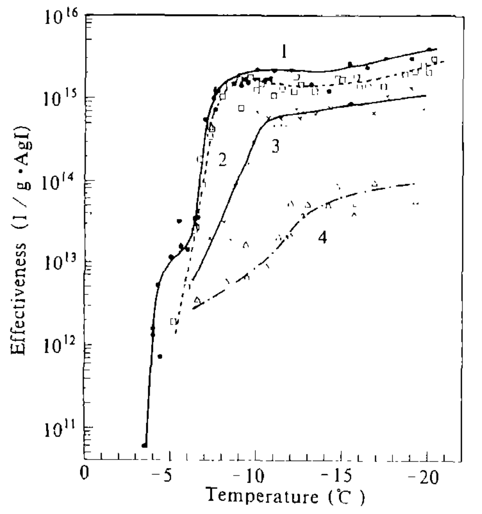

Fig. 4. Ice nucleating effectiveness tested in the 2 m^3 cloud chamber for four pyrotechnics. 1. BR–91–Y; 2. BR–88–5; 3. Silverspare; 4. TB–1.

higher than Silverspare and 50—200 times higher than TB–1. Particularly, BR–91–Y still has the effectiveness of 10^{13} / g (AgI) at –5°C, greater than other pyrotechnics at higher temperatures. The comparison is reasonable as all tests are conducted in the same chamber and under the same conditions.

The ice nucleating effectiveness of BR–91–Y pyrotechnic reported here has reached the level comparable with that of the AgI–acetone solution combustion systems which is beyond expectation. According to other previous work, the effectiveness of pyrotechnic was about two orders of magnitude lower than that of AgI–acetone systems. However, the AgI–acetone burner with two high efficient solution formulations has been also tested in the same cloud chamber (Feng et al. 1990) and the effectiveness versus temperature characteristics are given in Fig. 5 with that of BR–91–Y. It shows that the effectiveness of BR–91–Y is greater than AgI–acetone solution combustion systems at the temperature warmer than –12°C, and lower at the temperature below –12°C.

4. *Nucleating Rate*

In order to determine the ice nucleating rate of the pyrotechnics the method suggested by DeMott et al.(1983) is used. Figure 6 is the kinetic plots of ice crystal formation by four kinds of pyrotechnic aerosol. The average time (with all test temperatures) for 90% ice crystal nucleation (T90) is 22.6, 19.5, 21.2 and 4.7 min for TB–1, Silverspare, BR–88–5 and BR–91–Y, respectively. The nucleation rate of BR–91–Y is temperature dependent and the average time T90 is 8.6 min for temperature below –12°C while 3.4 min for temperature higher than –12°C. It is suggested that the aerosol produced by BR–91–Y is condensation–freezing ice nuclei which

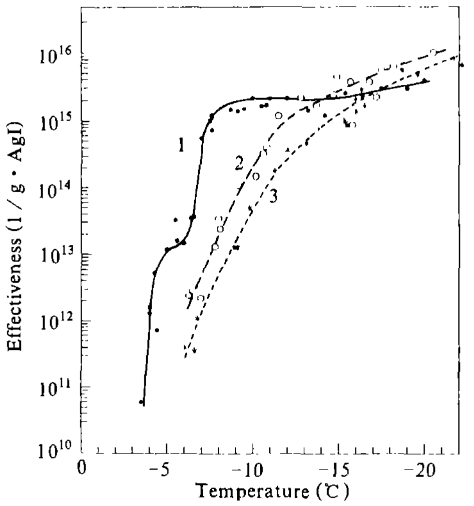

Fig. 5. Comparison of nucleating effectiveness between BR−91−Y pyrotechnic and AgI−acetone solution combustion systems. 1. BR−91−Y; 2. AgI • AgCl−NaCl; 3. AgI−NH_4I.

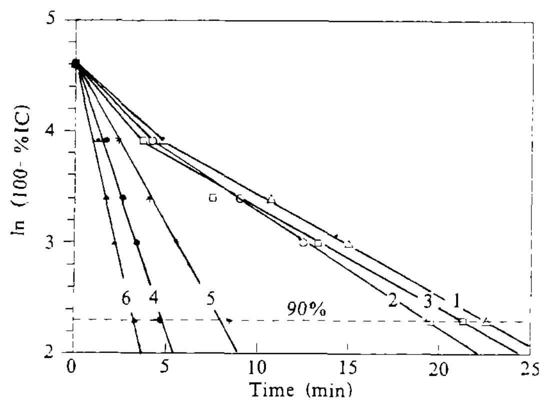

Fig. 6. Ice nucleating rate for four pyrotechnics. 1. TB−1; 2. Silverspare; 3. BR−88−5; 4. BR−91−Y; 5. BR−91−Y at temperature below −12°C; 6. BR−91−Y at temperature warmer than −12°C.

related to the water vapour and with very high nucleation rate.

VI. ANALYSIS OF AEROSOL NATURE

Many gases and aerosol particles are produced during the combustion of pyrotechnic, in which only the particles containing AgI can act as ice nuclei. To analyze their physical and chemical features is helpful to the understanding of the nucleation properties.

1. *The Neutron Activation Analysis of Elemental Composition*

The BR−91−Y pyrotechnic is combusted in a 10 m^3 room and the produced aerosols are collected using a special filter paper with low background elements. After 5 liters of aerosol containing air have been sampled, the filter is send to make neutron activation analysis by Institute of High Energy Physics, Chinese Academy of Sciences. The primary composition of the aerosol, ratio of mass and ratio of gram atomic weight are shown in Table 1. The results show that it is a multiphase aerosol system containing Ag, Cu, K, Na, I, Cl, and Br; the elements of K and Cl are the main composition. Na, Br and other negligible elements are not included in the formulation and they might be mixed up with other compounds used in making the pyrotechnic.

Table 1. Elemental Composition of the Aerosol Produced by BR−91−Y Pyrotechnic

Composition	Ag	Cu	K	Na	I	Cl	Br
Content ($\mu g / m^3$)	495	300	6650	1400	3250	7000	89
Ratio of mass	1	0.6	13.4	2.8	6.6	14.1	0.2
Ratio of gram atomic weight	1	1.03	37.2	13.3	5.6	43	0.25

2. *X–Ray Powder Analysis*

The aerosol produced by BR–91–Y is also collected using a 0.2 μm millipore filter, after tens of milligrams of powder obtained, then sent to the Central Iron and Steel Institute to make X–ray powder analysis. The aerosol powder with pure silicon powder is spread on the (531) plane of monocrystalline silicon slide to prepare the test samples (Lu 1986). The silicon powder is used to increase the analysis precision. The chemically pure AgI agent is crushed up and samples are also made with the same procedures. The measurements are carried out on Philips APD–10 X–ray diffractometer using Co–Kα radiation and the scanning speed of angle meter was $1^\circ / 8\ \mathrm{min}^{-1}$ (2θ). It is identified that AgI in the pyrotechnic aerosol has the hexagonal crystal structure and its lattice parameters are smaller than those of pure AgI agent and AgI+BiI_3 aerosol (Scott et al. 1989), having the closest match to ice (Table 2). The analysis also shows that the main composition of the aerosol is KCl with stronger diffraction peaks.

Table 2. The Lattice Parameters for BR–91–Y and AgI+BiI_3 Aerosol, Pure AgI and Ice

Sample	a axis	c axis	c / a	Discrepance with ice (%)		
				a	c	c / a
AgI*	4.5922	7.510	1.635	1.57	1.94	0.34
AgI agent	4.593	7.514	1.636	1.59	2.00	0.40
BR–91–Y	4.571	7.469	1.634	1.11	1.38	0.28
AgI+BiI_3**	4.583	7.493	1.635	1.37	1.71	0.34
Ice	4.521	7.367	1.630	0	0	0

* From International Center for Diffraction Data, Powder Diffraction File, Pennsylvania 19081, USA (1978), 9—374.

** Scoot et al.(1989).

3. *Size Distribution of Aerosol*

The aerosol produced by burning BR–91–Y is also collected on the substrate samples coated with carbon by an electrostatic precipitator. The particle size distribution is gotten from the transmission electron microscope pictures which is taken by Department of Physics, Peking University. All particles are in a size range from 0.025 to 0.4 μm with the mean cubic root diameter being 0.178 μm. The size of the aerosol produced by BR–91–Y is rather larger than those by other pyrotechnics measured by Sax et al.(1979) and Federer and Schneider (1981).

All these measurements provide the basic evidence to interpret the high nucleating effectiveness and nucleating rate for the aerosol produced by BR–91–Y pyrotechnic. The fact that AgI in the aerosol still keeps the hexagonal crystal form and has smaller lattice parameters which are very close to ice would lead to less strain and lower energy barrier during the epitaxial growth of ice. The multiphase aerosol with hygroscopic composition would make the aerosol nucleate through condensation–freezing mechanism to form ice at a high nucleating rate. The larger aerosol particle size might contribute to such a nucleating feature of BR–91–Y pyrotechnic, that the effectiveness is higher than other pyrotechnics at warmer temperature and almost not change as temperature below -10°C.

V. SUMMARY

With the nucleating properties mentioned before the aim of applying pyrotechnics to produce high efficient composite AgI ice nuclei has been achieved. The fact that new pyrotechnics have high ice nucleating effectiveness especially in warm temperature range would widen the cloud seeding limit (higher temperature and lower altitude) and therefore increase the seeding chance. The high nucleating rate of BR–91–Y is significant for seeding cumulus and hail cloud, for a bubble of those clouds often has only several minutes lifetime. The BR–91–Y is probably preferable to be used in stratiform cloud seeding. The new pyrotechnics would be very useful in weather modification.

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