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Study of the Influence of Magnesium Antimonide on the Formation of Ice Particles in a Supercooled Fog

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TRANSLATION OF

STUDY OF THE INFLUENCE OF MAGNESIUM ANTIMONIDE ON THE FORMATION OF ICE PARTICLES IN A SUPERCOOLED FOG

(Issledovanie vliianiia antimonida magniia na obrazovanie ledianykh chastits v pereokhlazhdennom vodnom tumane)

by

N. F. Gol'tiakov and P. N. Krasikov

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STUDY OF THE INFLUENCE OF MAGNESIUM ANTIMONIDE ON THE FORMATION OF ICE PARTICLES IN A SUPERCOOLED FOG

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In recent years, extensive studies have been devoted to the glaciative properties of various chemicals, in order to develop methods of dispersing supercooled fog or clouds and of inducing precipitation. Silver iodide (AgI) is the most effective substance of this kind. Ice particles begin to form at a temperature of -3° to -4° C in a supercooled fog seeded with AgI. However, AgI is relatively expensive and scarce, and it has a substantial drawback: The action of light and other factors quickly decomposes the AgI particles and eliminates their ice-forming properties.

Hence, many investigators have been prompted to look for other reagents of water crystallization. The choice of substances has been based mostly on the similarity between their crystal structures and that of ice. Other approaches to the selection of reagents have also been proposed [1], but we shall not discuss them here, since the results of these efforts are not yet clear.

The ice-forming properties of substances have been studied by R. Montmory [2], who based his preliminary estimate of a substance's effectiveness as an ice-crystallization reagent on the following postulates of L. Royez [3]:

1. The ease with which epitaxy (oriented growth of a crystal on the crystal base) can be achieved depends on the similarity of the lattice parameters.

2. Not all the lattice points in the composition plane need coincide in order to attain epitaxy.

Table 1, taken from [2], shows several substances whose lattice parameters are very similar to those of ice.

Table 1

Lattice parameters of five substances

Substance	a_0 (Å)	Δa_0	C_0 (Å)	ΔC_0	Symmetry group
Ice (0° C)	4,5135		7,3521		D^4_{6h} (at -20° C)
AgI	4,580	+0,0665	7,494	+0,1419	C^4_{6v}
PbI_2	4,54	+0,0265	6,68	−0,4921	D^3_{3d}
Mg_3Sb_2	4,573	+0,0595	7,229	−0,1231	D^3_{3d}
MgTe	4,52	+0,0065	7,33	−0,0221	C^4_{6v}

On the basis of these data, Montmory [2] presumed that MgTe (magnesium telluride) would be the most active, and Mg_3Sb_2 (magnesium antimonide) the second most active, crystallization reagent for supercooled fog particles.

Montmory performed laboratory experiments to study the ice-forming properties of Mg_3Sb_2 and found that it induced ice-particle formation in supercooled fog at temperatures as high as -2.5 to -4° C. However, he remarked [2] that the resulting data are highly tentative. Unfortunately, Montmory gave no information on methods of obtaining Mg_3Sb_2, but simply mentioned that it was prepared by direct alloying of magnesium and antimony in their stoichiometric ratio. What is more, his paper did not contain a description of the experimental procedure.

We have tried to evaluate the ice-forming properties of Mg_3Sb_2 on the basis of experiments in a cold chamber.

Production of Magnesium Antimonide

The literature on Mg_3Sb_2 is very limited. It was produced by G. Grube and R. Bornak by direct alloying of magnesium and antimony [3]. It is very difficult to prepare Mg_3Sb_2, mainly because magnesium is very active.

We obtained Mg_3Sb_2 for our experiments at the Ferrous Electrometallurgy Laboratory of the M. I. Kalinin Polytechnic Institute.

We used a mixture of magnesium and antimony in their stoichiometric ratio: 23 parts Mg and 77 parts Sb, by weight.

Magnesium is a silvery-white metal with a melting point of 651° C, a boiling point of 1120° C, and it has a hexagonal crystal lattice.

Antimony is a silvery-white metal with a melting point of 630° C, a boiling point of 1440° C, and it crystallizes in rhombohedra.

Several attempts to alloy Mg and Sb in an electric vacuum furnace (at a vacuum of about 10^{-4} mm Hg) at temperatures of 900 to 1200° C ended in failure. At about 950° C, there is a very violent reaction similar to an explosion. The substances combine with a great heat effect, which raises the temperature 300 to 400° C [5]. *)

As a result of the discharge during the reaction and cracking of the corundite crucible, no combination of the substances could be detected in it (following cooling of the furnace); the crucible was empty. This recurred several times.

We tried to obtain the Mg_3Sb_2 compound under a flux consisting of magnesium chloride ($MgCl_2$) and potassium chloride (KCl) by melting over a gas burner (at a temperature of about 700 to 800° C), but again without success. We cracked open the graphite crucible after it had cooled, but the alloy was inhomogeneous and broke down into the two components when tapped lightly. No reaction occurred, apparently because the temperature was not high enough.

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*) The list of references contains no [5]. Probably this should be [4][Tr. note].

Next, we melted 50 g of the magnesium-antimony mixture in a high-frequency electric furnace, using a pointed graphite crucible that had been pre-heated in vacuum. The mixture of metals was heated in an atmosphere of pure argon at a pressure of about 100 mm Hg until a bright flash was seen through the furnace window and part of the material was discharged from the crucible. After cooling and breaking the crucible, we found a small cylinder of Mg_3Sb_2 weighing 44 g, which we immersed in machine oil to prevent oxidation.

The resulting compound was friable, and the cylinder split in two when struck with a hammer. The fracture plane clearly showed the compound had a uniform crystalline structure with relatively large particles.

It had been shown in [3] that Mg_3Sb_2 exists in two variants: One of them has a hexagonal lattice structure and the other, a cubical structure. We did not determine which variant we had obtained, since we are not concerned with crystallographic studies.

Laboratory Experiments

Our experiments for determining the properties of Mg_3Sb_2 as a crystallization nucleus were made in the cold chamber of the A. I. Voeikov Main Geophysical Observatory.

The cold chamber is a thick-walled cabinet lined with a thermal insulator 0.4 m thick. The effective volume of the chamber is $0.7 \times 0.6 \times 0.6 = 0.25\ m^3$. Ammonia circulates through coils between the insulation and the inner wall of the chamber. An ammonia compressor cools the chamber to -25° C. The inner walls of the chamber are covered with galvanized iron and are coated with black oil-based paint.

A double heat-insulating panel with double glass windows and connection pipes with plugs in the opening of the chamber was installed for observing the processes inside the chamber

when reagents were introduced, for taking fog-droplet samples, and for illuminating the chamber. Calcium chloride was placed in the space between the double panes as a dessicant to keep the windows from fogging. The supercooled fog was created by bringing vapor from an electric boiler into the chamber. The temperature in the chamber was measured with a mercury thermometer. The experiments were conducted after the ammonia compressor and fan had been turned off, beginning at the lowest temperatures and continuing to higher temperatures as the air in the chamber warmed up.

A microscope-camera setup was used to photomicrograph the supercooled fog droplets and crystals. The droplets were caught on slides coated with a thin film of a machine oil and vaseline mixture, and the crystals were caught on slides coated with a thin film of lacquer. After the ice crystals had melted and the water had evaporated, their imprints (replicas) remained on the lacquer, and we photographed them.

The experiments were performed in the following order:

A supercooled fog was created in the precooled chamber and the temperature was noted. Next, the reagent was introduced and the appearance of the crystals was made visible in the beam of an electric light.

Fifty-seven experiments were made with the Mg_3Sb_2 at temperatures from -18 to -6° C.

Various methods were used to introduce the reagent into the supercooled fog.

According to the diagram of state in [3], the melting point of the compound is about 1228° C. Therefore, we employed an electric arc in our first experiments. Before the experiment, the Mg_3Sb_2 was taken out of the oil, washed in gasoline, and ground in an agate mortar to an average granule size of about

1 mm. Then a few milligrams of this powder were poured into an indentation which had been drilled in one of the carbons.

The arc was sparked in the supercooled fog inside the chamber. Three such experiments, at temperatures from -16 to -13° C, failed to yield any positive result, i.e., no crystallization was noted.

In several experiments, we used a vessel made of hard glass in the shape of a truncated cone. The ground Mg_3Sb_2 was poured into the vessel. The heat was supplied by a spiral electric element wound around the vessel (fig. 1). In one of the three experiments, we obtained a striking effect at a temperature of -16.4° in the fog. The vessel with the heating element was put into the chamber, heated to white heat, and removed. (No smoke was visible during heating.) After 1 to 2 min, we saw crystals which rapidly grew in size and number. Within a few minutes, the entire fog had been completely crystallized. In the following experiment, crystals appeared again, but in substantially smaller quantity.

Next, we used a porcelain tube as the sublimation device; it was about 5 cm long and 4 mm in inside diameter. A platinum ribbon 0.7 mm thick was wound around the tube (fig. 2). We obtained a very good result in one of seven experiments using this heating element: Complete crystallization occurred at a temperature of -13° C.

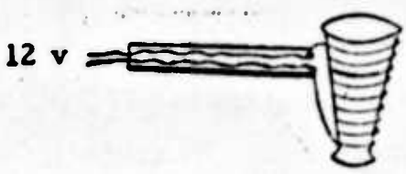

Figure 1

Figure 2

Assuming that the heating was not sufficient, we put the platinum ribbon inside the tube and plugged it with mica.

In experiments with this device, a pronounced effect was obtained only at a temperature of -18° C.

It should be noted that in this experiment the Mg_3Sb_2 had not been washed in gasoline, and in our opinion, the oil film provided some protection against oxidation before sublimation. The oil burned off during the experiment without affecting the result appreciably.

In the nine subsequent experiments, we again employed the electric arc. We placed larger crystals of Mg_3Sb_2 in the gap, hoping that if the surface of the crystal oxidized, the inner, unoxidized portion of the crystal would evaporate when the arc was sparked. In several experiments, we fastened the crystal to one of the carbons and created an arc between the crystal and the other carbon (fig. 3). We obtained a positive effect in two experiments at temperatures of -15.2 and -14.5° C: A considerable quantity of crystals was noted after the arc was sparked.

In several subsequent experiments, we created an arc between two crystals to eliminate the effect of the carbons as much as possible (fig. 4). In several such experiments, we observed effective crystallization at a temperature of about -14° C.

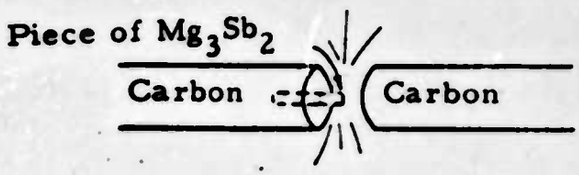

Figure 3

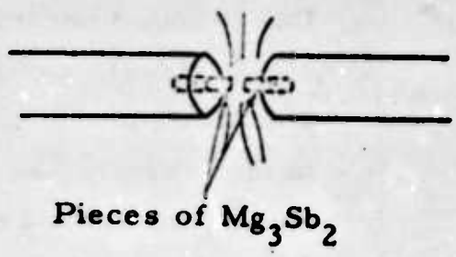

Figure 4

We employed an electric arc between two carbons in six experiments. One arc was flat, but we made an indentation in the other and pressed the ground reagent (Mg_3Sb_2) into it, not allowing it to project beyond the face of the carbon (fig. 5). This provided a minimum access of air to the reagent during sublimation. All six experiments yielded positive results in

the temperature interval from -17 to -10.5° C. The most effective crystallization was observed at -17 and -14° C, with formation of hexagonal platelets, while at -12° C, the result was less impressive and the crystals were smaller. At temperatures close to -10.5° C, considerably fewer crystals formed and we could not get any samples for photomicrography. No crystallization was noted at higher temperatures.

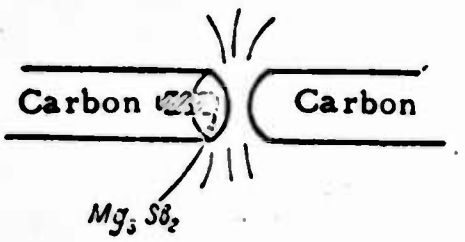

Figure 5

In two experiments, we introduced a finely ground powder of Mg_3Sb_2 into the supercooled fog by means of an air jet. The results of these experiments were negative. We also tried spraying an aqueous suspension of Mg_3Sb_2 into the fog. A thin powder of the substance was shaken up in water. The suspension was introduced into the chamber by an atomizer. We made 17 experiments with this suspension and got a positive result in 11 of them, i.e., we noted crystallization after spraying the suspension. It should be noted that in these experiments the ice crystals formed somewhat more slowly than in sublimation of Mg_3Sb_2, but they were larger and precipitated more rapidly. We conducted the experiments in the temperature interval -12 to -6° C. As a rule, -8.5° C can be considered the maximum crystallization temperature, i.e., the maximum is higher than in sublimation of Mg_3Sb_2 (-10.5° C). This difference can probably be explained as follows: When Mg_3Sb_2 (an unstable substance) is sublimed, it oxidizes and decomposes. Therefore, there is no assurance that this method of seeding the fog with Mg_3Sb_2 involves mostly nuclei of this particular substance. It is quite probable that oxides of the component metals (e.g., MgO) are formed. According to data in [1], MgO particles are not effective

crystallization nuclei at temperatures above -18° C. Solid particles of Mg_3Sb_2 are found in the droplets which form when the suspension is sprayed into the fog. We know from the literature that water with heavy aerosols suspended in it has a higher freezing point than pure water. Aerosols, whose crystalline structure is similar to that of ice, affect the freezing point of water greatly. Consequently, the droplets of Mg_3Sb_2 suspension introduced into the supercooled fog freeze at a determinate temperature and instigate the ice phase, which crystallizes the fog.

Conclusion

Our laboratory experiments to test Mg_3Sb_2 as a reagent of crystallization of water have shown that when this substance sublimes in a supercooled fog, the upper temperature limit for the occurrence of the ice phase is about -10 to -11° C. The temperature limit increases to -8° or -9° C when Mg_3Sb_2 in aqueous suspension is sprayed into the fog.

Hence, Mg_3Sb_2 is, basically, an effective reagent for crystallizing a supercooled fog. However, there are some practical difficulties involved in employing this substance, e.g.: the instability of the substance and the difficulty of producing and dispersing it.

Our results are tentative in nature and require additional experimental verification.

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