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TECHNOLOGY OF INORGANIC
SUBSTANCES AND MATERIALS

Phase Equilibria in Water-Salt Systems Consisting of Potassium, Sodium, and Ammonium Carbonates and Anti-Icing Properties of Carbonate Compositions

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Abstract—Phase equilibria in K_2CO_3–H_2O, Na_2CO_3–H_2O, K_2CO_3–Na_2CO_3–H_2O, K_2CO_3–$(NH_4)_2CO_3$–H_2O systems under temperatures ranging from 0 down to −36°C are investigated. The carbonate compositions forming low-temperature eutectics are revealed. Their melting ability with respect to ice under temperatures −5 and −10°C is determined. It was found that potassium carbonate is characterized by sufficient anti-icing properties. Potassium carbonate composition activity is determined with respect to metals. Efficient corrosion inhibiters are selected. It was found that potassium carbonate is aggressive with respect to cement concrete. Special protection is necessary, if potassium carbonate is used on cement concrete coatings.

Keywords: water-salt systems, phase equilibria, potassium, sodium, ammonium carbonates, anti-icing compositions

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INTRODUCTION

New anti-icing reagents based on salt compositions are investigated in the present work, which is the continuation of [1, 2], where phase equilibria in water-salt systems are studied. Several nitrate and acetate compositions, promising as a base of anti-icing reagents, have been found. Phase equilibria in water-salt systems containing sodium, potassium and ammonium carbonates for temperatures ranging from 0 down to 36°C are investigated. It is revealed that salt compositions form low-temperature eutectics with ice. The results of the study are presented in the paper.

The main tasks of the present paper are as follows:

1. To reveal salt compositions forming low-temperature eutectics with ice in binary water-salt systems of water-salt types and in triple systems of the salt-water type, to determine eutectics temperatures and compositions by investigating phase equilibria for temperatures ranging from 0 down to –36°C.

2. To determine the melting ability of salt compositions with respect to ice under temperatures −5 and −10°C.

3. To determine corrosion activity of potassium carbonate solutions with respect to metals and alloys and to select corrosion inhibiters.

4. To investigate how potassium carbonate solution impacts cement concrete.

EXPERIMENTAL

Potassium, sodium, and ammonium carbonates of analytically pure quality are used as the initial substances for investigating phase equilibria in water-salt systems. Phase equilibria in K_2CO_3–Na_2CO_3–H_2O, K_2CO_3–$(NH_4)_2CO_3$–H_2O systems with different ratio between salt components under temperatures ranges from 0 down to −36°C are investigated for revealing the low temperature eutectics. The studies are performed by visual-polythermal method [1] and liquid nitrogen is used as a coolant. The melting ability of salt compositions with respect to ice is calculated according to melting (crystallization) types by using the following formula: $A = (100 - C_1)/C_1$, where A is the melting ability of the salt composition at a certain temperature, C_1 is a salt concentration in the solution at this temperature.

Table 1. Anti-icing properties of metal carbonates and of carbonate compositions

№	Systems	Eutectics parameters		Melting ability with respect to ice, g/g	
		concentration, % (mass)	temperature, °C	at −5°C	at −10°C
1	$K_2CO_3—H_2O$	41.0	−36.0	5.6	3.3
2	$Na_2CO_3—H_2O$	6.0	−2.5	—	—
3	$(NH_4)_2CO_3—H_2O$	10.0	−5.0	—	—
4	$K_2CO_3 + Na_2CO_3$ (3 : 1)—H_2O	37.0	−18.0	5.2	2.7
5	$K_2CO_3 + Na_2CO_3$ (2 : 1)—H_2O	25.0	−12.0	6.0	3.3
6	$K_2CO_3 + (NH_4)_2CO_3$ (3 : 1)—H_2O	27.0	−13.0	6.7	3.3
7	$K_2CO_3 + (NH_4)_2CO_3$ (2 : 1)—H_2O	23.0	−10.5	6.7	3.5

RESULTS AND DISCUSSION

1. Phase Equilibria in K_2CO_3–Na_2CO_3–H_2O, K_2CO_3–$(NH_4)_2CO_3$–H_2O Systems

Table 1 depicts the results of the study for phase equilibria in the systems including the information on eutectics composition and temperature and on the melting ability of different carbonate compositions with respect to ice at temperatures of −5 and −10°C.

From Table 1 it is seen that it is of interest to examine potassium carbonate and its mixture with sodium carbonate (3 : 1) as the anti-icing reagents. Other mixtures are not characterized by the needed anti-icing properties. Potassium carbonate forms the low-temperature eutectic (−36°C) with ice and it is characterized by sufficient melting ability with respect to ice. It is necessary to determine potassium carbonate corrosion activity against metals and cement concrete, if we are going to use it as the anti-icing reagent.

2. Corrosion Tests

The aim of the corrosion test is as follows: to determine corrosion impact caused by potassium carbonate to metals and alloys. In the present work, we use two test procedures according to the Russian Industrial Standard (OST) 190257.

(1) Metallic samples are completely immersed in the test solution (20% potassium carbonate solution with a density of 1.189 g/cm^3, pH 11.5−12.0) for one hour at a room temperature of 20°C and are weighed before and after tests.

(2) The samples are immersed in the test solution for one hour. After the testing procedure, one half of the samples are washed with distilled water and dried by compressed air. The other half of the samples was not washed. The reference samples are not processed by the test solution. All samples are put into a humidity chamber for 30 days at room temperature. Periodically, samples are inspected: within the first five days they are inspected daily and after that they are inspected each five days to the end of the tests.

How the test solution acts on metals is estimated according to samples' mass variation g/(m^2 h), (Russian State Standard (GOST) 9.909) and according to external appearance variation within the testing period. The variation in the samples' external appearance is estimated just after processing in the test solution and after 30 days in the humidity chamber. Products of aluminum alloy corrosion are removed in a 30% solution of nitric acid for three minutes at room temperature; products of zinc and cadmium coating corrosion are removed in 10% ammonium chloride solution at 70°C for five minutes; products of structure steel 30KhGSA corrosion are removed by VPT-1 paste produced by All-Russian Scientific Research Institute of Aviation Materials according to Russian Technical Recommendations (TR) 1.595-337-2003.

The following metallic materials are tested: aluminum alloy D16T (not anodized, not plated); aluminum alloy D16AT (plated), aluminum alloy V95AT (plated); aluminum alloy D16AT with a protective anode-oxide coating with a filling of chromic acid (An. Ox.fch. coating); carbon structure steel 30KhGSA (chemically plated); cadmium coating Kd6.khr on steel 30KhGSA; zinc coating Ts9.khr on steel 30KhGSA. Complete immersion according to the first procedure shows that samples processed in the test solution for one hour activates corrosion of all tested metallic materials. The corrosion impact is the greatest for aluminum alloys D16T, D16AT, V95AT and D16AT with a protective anode-oxide coating with a filling of chromic acid: mass loss of the samples is higher by several times than the maximum permissible value according to Russian Branch Standard (OST) 54-0-830.74-99 for aviation materials. Mass loss for the samples made of carbon steel and for their cadmium and zinc coatings after processing in potassium carbonate solution is higher than the maximum permissible value for cadmium coating on steel 30KhGSA by 0.28−0.42 g/(m^2 h). Tests performed in the humidity chamber show that if samples are prelim-

Table 2. Corrosion tests results for the samples after complete immersion into 20% solution of potassium carbonate

Material grade	Mass loss rate after complete immersion in 20% solution of potassium carbonate, g/(m^2 h)		
	without inhibitor	with inhibitor Maklor A	with inhibitor KI-1MR
Aluminum alloy	−2.07	−1.18	−0.35
D16T, unplated	−2.20	−1.45	−0.17
Aluminum alloy	−1.40	−0.73	−0.20
D16T, plated	−1.47	−0.80	−0.20
Aluminum alloy	−0.10	−0.23	+0.03
D16T with protecting anode-oxide coating with filling in chromic acid	−0.12	−0.02	+0.02
Aluminum alloy	−1.32	−0.76	−0.19
V95AT, plated	−1.31	—	−0.16
Cadmium coating	−0.42	−0.28	−0.08
on steel 30KhGSA	−0.28	−0.58	−0.10
Zinc coating	−0.13	−0.02	−0.05
on steel 30KhGSA	−0.13	−0.02	−0.18
Structure steel	+	0.00	+0.07
30KhGSA	+ (corrosion products of ginger (red) color are distributed uniformly over sample's surface)	−0.02	0.00

Table 3. Specific volume loss of cement concrete surface layer

№	Reagent's name	Volume loss for the samples (averaged over series), cm^3/cm^2 for the number of freezing–unfreezing cycles					
		25	50	75	100	125	150
1	Carbamide	0.002	0.004	0.045	0.09	0.105	0.21
2	K_2CO_3	0.001	0.003	0.032	0.059	0.12	0.26

inarily processed in the test solution, even with further washing, make their corrosion state worse with respect to reference samples. Residual reagent present on the sample surface also worsens their corrosion state with respect to the reference samples. The surfaces of all samples tested in the humidity chamber for 30 days are destroyed by corrosion.

Thus, the results of these tests show that the solution of potassium carbonate is corrosively active with respect to all tested metallic materials. We select corrosion inhibitors for decreasing the corrosion activity of potassium carbonate solution. The following inhibitors are tested: KI-1MR and inhibitor MALKOR A produced by the scientific enterprise Tekhnopribor. From Table 2, it is seen that the corrosion activity of a test 20% solution of potassium carbonate decreases if inhibitors KI-1MR or MALKOR A produced by Tekhnopribor, with a concentration of 1.0%, are introduced into solution.

3. Potassium Carbonate Impact on Cement Concrete

The corrosion activity of potassium carbonate is determined with respect to cement concrete (Figs. 1–3). Tests are performed with respect to carbamide according to the procedure presented in the Russian Branch Standard (OST) 54-0-830-74-99 "Civil reagents for preventing ice formation on artificial coatings. Technical requirements". The test procedure is described

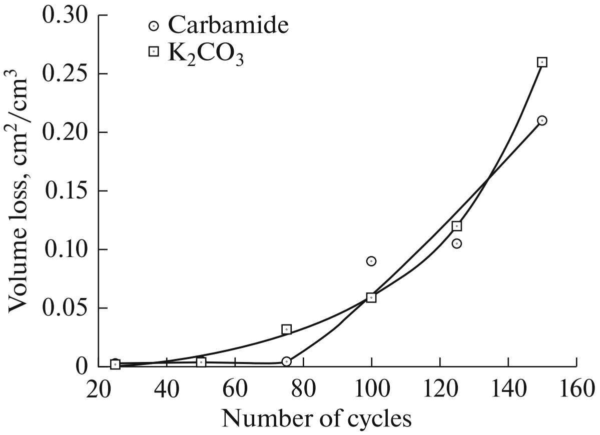

Fig. 1. The relationship between specific volume loss of cement concrete samples and the number of freezing-unfreezing cycles.

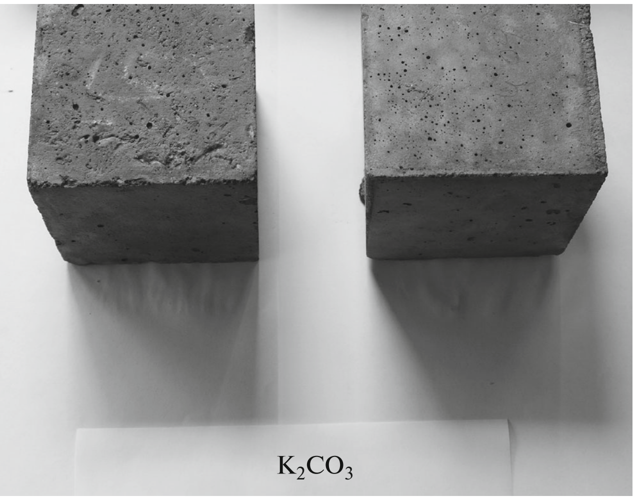

Fig. 2. State of cement concrete samples before tests.

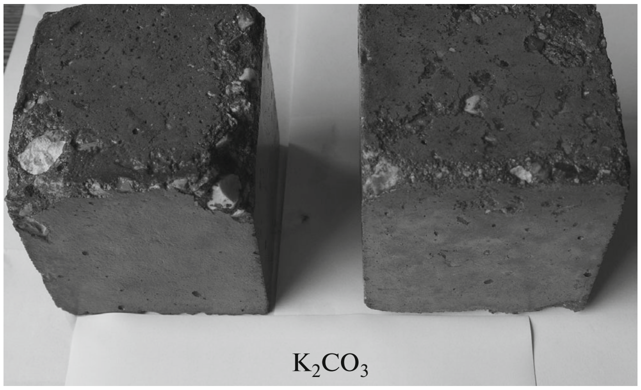

Fig. 3. State of cement concrete samples after 80 freezing-unfreezing cycles in 5% solution of K_2CO_3.

in detail in [2]. Potassium carbonate aggressiveness with respect to concrete is calculated according to specific volume loss of cement concrete samples by using the following formula: Πa = M/Ma, where M is a number of freezing-unfreezing cycles, which decreases by 0.04 cm^3/cm^2 the volume of concrete sample in carbamide solution (Table 3); Ma is the number of cycles caused the same volume loss of concrete sample in 5% potassium carbonate. The reagent can be used, if the aggressiveness Πa is not higher than 0.8. From the results of the study it may be seen that the aggressiveness of potassium carbonate solution is higher than the standard value (Πa = 73/83 = 0.88) and it means that it is aggressive with respect to cement concrete. That is why, if potassium carbonate is used as anti-icing reagent on concrete surfaces, it is necessary to use special protective measures (for example, to introduce surface-active substances into reagent composition).

CONCLUSIONS

(1) Phase equilibria in K_2CO_3–H_2O, Na_2CO_3–H_2O, K_2CO_3–Na_2CO_3–H_2O, K_2CO_3–$(NH_4)_2CO_3$–H_2O systems at temperatures ranging from 0 to −36°C were studied. It was found that only potassium carbonate is characterized by sufficient anti-icing properties, by a low-temperature eutectic (–36°C) and by sufficient melting ability with respect to ice (5.6 g/g under temperature −5°C). Additions in the form of sodium and ammonium carbonates spoil anti-icing properties of the reagents.

(2) The corrosion activity of potassium carbonate solution with respect to metals and alloys was studied. It was found that potassium carbonate solution is corrosively active with respect to all studied metallic materials. The corrosion activity of potassium carbonate solution can be reduced to normalized values, if inhibitors KI-1MR or MALKOR A produced by Tekhnopribor are introduced with concentration of 1.0%.

(3) It was found that potassium carbonate is aggressive with respect to cement concrete, and if it is used as the anti-icing reagent on cement concrete coatings, special protective means should be used.

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