COMPOSITION OF THE ATMOSPHERIC CORROSION PRODUCTS OF ALUMINUM

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The literature gives much information on the phase composition of the atmospheric corrosion products of aluminum and its alloys, but in most cases it is conflicting [1, 2]. This is due largely to the fact that field tests performed in different climatic and meteorological conditions do not take account of the true length of the corrosion process or the different degrees of atmospheric pollution by corrosive gases.

We have made an attempt to determine the phase composition and thermal stability of the atmospheric corrosion products of aluminum under various field test conditions.

Specimens of A-7 aluminum, obtained by continuous casting [3], were investigated. The climatic and meteorological characteristics of the test regions were assessed from the wetting times of the metal surfaces [4]. The atmosphere of the test regions was contaminated by sulfur dioxide, the concentration of which was measured monthly by the linear-colorimetric method [5]. Table 1 gives the characteristics of the test regions.

The phase composition and thermal stability of the powdered atmospheric corrosion products of aluminum were assessed 2 years after the tests began. The composition and ratio of the components in the mixture of corrosion products were determined by x-ray and IR spectroscopic analysis; the thermal stability was investigated by the thermogravimetric method. The x-ray diffraction patterns of the powders were recorded in a DRON-1 diffractometer in Fe K_α radiation with a manganese filter. The IR spectra were recorded in a UR-10 spectrophotometer in the 400-4000 cm^{-1} region; for this purpose a suspension of the corrosion products in Vaseline oil was prepared [6]. The thermograms were recorded in a Kurnakov pyrometer designed by the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR.

According to the x-ray phase analysis data, the composition of the atmospheric corrosion products of aluminum of the different regions was virtually the same. Table 2 gives the results of calculation of the most typical x-ray diffraction pattern (for region A).

TABLE 1. Corrosion Field Test Regions

Region	Metal surface wetting time, h/year	SO_2 content of atmosphere, mg/m^3*
A	1700	0,25
B	1250	0,13
C	2000	Traces

*The values given are the mean SO_2 concentrations; the SO_2 concentration varied by 10-20% during a year.

It will be seen that the atmospheric corrosion products of aluminum consist of $Al(OH)_3$, α-Al_2O_3, and high-temperature γ-Al_2O_3.

For the IR spectra of this specimen (Fig. 1), a comparison of the absorption bands with literature data revealed that the bands with ν = 3570 and 3300 cm^{-1} are due to valence vibrations of the hydroxyl ion [7] and the hydrogen bond in crystallized aluminum hydroxide [8]. The broad band at 765-1070 cm^{-1} is due to deformation and libration vibrations of the Al–O bond in aluminum hydroxide and oxides [8], while the frequency ν = 3450 cm^{-1} corresponds to valence vibrations of the Al–O bond in Al_2O_3 [9]. Thus the data confirm the presence of $Al(OH)_3$ and Al_2O_3 in the corrosion products.

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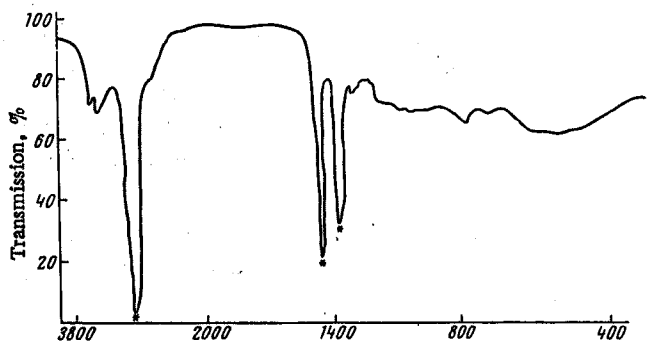

Fig. 1

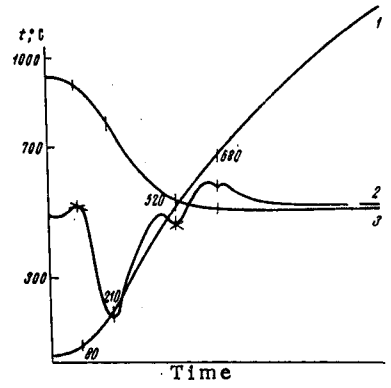

Fig. 2

Fig. 1. Thermogram of atmospheric corrosion products of aluminum in region A (denotes the absorption bands of Vaseline oil).

Fig. 2. Thermogram of the atmospheric corrosion products of aluminum in region B: 1) t, °C; 2) t, °C; 3) loss in weight, g.

TABLE 2. X-Ray Diffraction Pattern of Corrosion Products of Aluminum in Region A

Experimental data		Reference data		Compounds identified
d, Å	I_c, %	d, Å	I_c, %	
4,70	100	4,70	100	$Al(OH)_3$
4,27	30	4,31	40	"
3,60	20	3,60	30	"
3,45	15	3,44	20	"
3,19	20	3,19	41	"
2,70	5	2,71	10	
2,59	15	2,59	20	High-temperature γ-Al_2O_3
2,08	20	2,08	100	α-Al_2O_3
1,91	5	1,91	3	$Al(OH)_3$
1,50	5	1,50	13	High-temperature γ-Al_2O_3
1,40	30	1,40	100	The same
1,32	20	1,33	50	$Al(OH)_3$
1,17	5	1,176	10	High-temperature γ-Al_2O_3

TABLE 3. Composition of the Atmospheric Corrosion Products of Aluminum in the Different Test Regions

Region	Phase composition of the corrosion products	Content of components in the mixture, %	Region	Phase composition of the corrosion products	Content of components in the mixture, %
A	$Al(OH)_3$	60—80	B	$Al(OH)_3$	30—60
	γ-Al_2O_3	15—30		γ-Al_2O_3	30—60
	α-Al_2O_3	5—10		α-Al_2O_3	5—10
	$Al_2(SO_4)_3$	1		$Al_2(SO_4)_3$	1
			C	$Al(OH)_3$	15—30
				γ-Al_2O_3	60—80
				α-Al_2O_3	5—10

Furthermore, a detailed analysis of the IR absorption spectra of the different modifications of aluminum oxide [10] enables one to assert that the corrosion products do contain α- and γ-Al_2O_3.

The spectrum exhibits a weak band frequency 1115 cm^{-1}, which can be assigned only to valence vibrations of the SO_4^{2-} group [11]. This indicates the presence of $Al_2(SO_4)_3$ in the corrosion products; this was confirmed by chemical microanalysis.

The use of both analysis methods also enabled us to establish the quantitative ratios between the individual components in the mixture of corrosion products (Table 3).

The difference between the content of the components can be explained by taking account of the protective properties of γ-Al_2O_3, which is formed on the surface as the cast metal cools in the mold. In the atmosphere of region B the oxide film does not disintegrate much; as a result of interaction with water vapor and of electrochemical processes, this film is slowly converted to $Al(OH)_3$. In the presence of SO_2 the surface film of the electrolyte has an acid character. Under these conditions γ-Al_2O_3 breaks up far more rapidly, which intensifies corrosion and reduces the γ-Al_2O_3 content. The small amounts of $Al_2(SO_4)_3$ in the corrosion products may be attributed to periodic washing away of the salt from the surface by atmospheric precipitation.

The thermogram of the corrosion products of aluminum in region B (Fig. 2) exhibits the following endoeffects: t = 80°C, due to removal of hygroscopic and adsorbed water and to dehydration of $Al_2(SO_4)_3 \cdot 18H_2O$ as follows [12]:

$$Al_2(SO_4)_3 \cdot 18H_2O = Al_2(SO_4)_3 + 18H_2O; \quad (1)$$

t = 210°C, due to decomposition of aluminum trihydroxide as follows [13]:

$$Al(OH)_3 = \gamma\text{-}AlOOH + H_2O; \quad (2)$$

t = 520°C, due to decomposition of boehmite, formed by reaction (2) [14]:

$$2\gamma\text{-}AlOOH = Al_2O_3 + H_2O. \quad (3)$$

An analysis of the thermograms of the corrosion products after tests in all three regions enabled us to make an additional calculation of the $Al(OH)_3$ content. The results of this calculation agree closely with the data of Table 3.

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