ATMOSPHERIC CORROSION OF THALLIUM

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UDC 620.193.2

Information on the mechanism of the atmospheric corrosion of thallium is contradictory. According to some data [1], the process of atmospheric corrosion at a low relative air humidity is controlled by the reaction of thallium with water vapors, while at a high relative humidity it is controlled by hydration of Tl_2O, according to other data [2], thallium does not react with water in the absence of oxygen at 25°C.

Before the experiment plates of thallium (Tl 99.99%; Pb 0.003; Zn 0.003; Cu and Fe < 0.001%) with dimensions 20 × 40 × 3 mm were cleaned with a sharp steel chisel until the appearance of luster, then washed with distilled water and dried with filter paper. After weighing, the plates were set up on edge in glass weighing bottles and placed in desiccators, onto the bottom of which aqueous glycerin solutions were poured to maintain a set relative humidity. The temperature was maintained with an accuracy of ± 0.5°C; constancy of the concentration of aggressive gases and renewal of the atmosphere were provided for.

In determining the weight gain (g, g/cm^2), five samples were set up for each test, while in the determination of the amount of corrosion products (p, g/cm^2) 10 to 15 samples were used, of which two to three samples were selected periodically for analysis. The corrosion products were removed in 20% acetic acid, dissolving the compounds of univalent thallium and loosening the film, which after this is readily removed mechanically. Aqua regia was added to the solution with precipitate of Tl^{3+} compounds until the precipitate

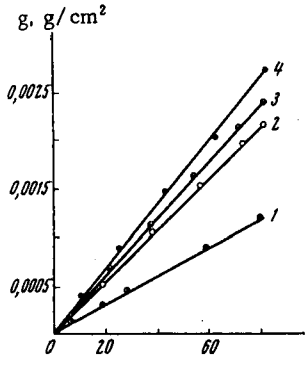

Fig. 1

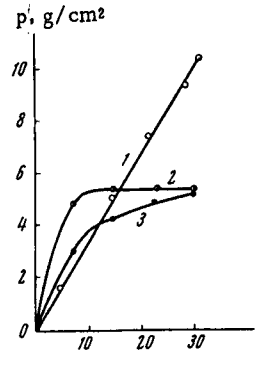

Fig. 2

Fig. 1. Change in the weight gain with time at 20°C. Relative air humidity (%): 1) 40; 2) 74; 3) 85; 4) 95.

Fig. 2. Influence of corrosion-active gases on the atmospheric corrosion of thallium at 20°C and relative air humidity 74%. 1) Air; 2) 0.01 mg/liter SO_2; 3) 0.01 mg/liter H_2S.

Translated from Zashchita Metallov, Vol. 6, No. 4, pp. 444-447, July-August, 1970. Original article submitted December 12, 1968.

TABLE 1. Dependence of the Rate of Atmospheric Corrosion on the Temperature and Relative Air Humidity

Relative humidity, %	Corrosion rate, g/cm²·day·10⁴		
	20°	30°	45°
40	2,2	—	—
74	4,0	6,2	11,2
85	4,4	6,6	12,5
95	5,0	7,1	15,3

TABLE 2. Ratio of the Amounts of Tl^+ and Tl^{3+} Compounds in the Corrosion Products

Temperature, °C	Relative humidity, %		
	74	85	95
		Ratio	Tl^+/Tl^{3+}
30	18,7	14,7	15,5
45	5,7	6,1	5,1

dissolved entirely. The solution obtained was treated with sulfuric acid (1:1) and evaporated until the liberation of SO_3 vapors. Ammonium persulfate was added to the solution, removing the excess by heating for several minutes. After cooling of the solution, a trilonometric titration was performed [3].

The x-ray diffraction pictures of the corrosion products were taken on an URS-60 apparatus according to the Debye — Sherer method in CuK_α radiation with a nickel filter.

At the temperatures studied (20-45°C), the rate of atmospheric corrosion of thallium increases with increasing relative atmospheric humidity, and does not change with time (Fig. 1), i.e., the products formed do not protect the metal from further corrosion [4, 5]. After prolonged exposure (60-80 days) at temperatures greater than 30°C, a gradual deviation from a linear dependence is observed.

The atmospheric corrosion of thallium proceeds at an appreciable rate even at very low air humidities, which is evidently due to the great hygroscopic properties of the corrosion products.

The rates of atmospheric corrosion of thallium were calculated according to the results of a quantitative analysis of the corrosion products (Table 1).

The rate of atmospheric corrosion of thallium increases as a linear function of the temperature; the temperature coefficient of the corrosion rate $k_t = (3.2 \pm 0.8) \cdot 10^{-5}$ g/cm²·day·°C.

In the presence of SO_2 and H_2S (Fig. 2) in the initial stage of the process the corrosion rate increases, but then decreases comparatively rapidly and falls almost to zero. The initial acceleration is evidently caused by an intensification both of anodic and of cathodic processes [4]. Subsequently, as corrosion products are accumulated on the surface, a protective film is formed, and corrosion decreases. The limiting value of the losses does not depend on the nature of the corrosion-active gas, and in the presence of SO_2 it is reached more rapidly than in the presence of H_2S, since in the first case, as a result of the greater aggressiveness of SO_2, the protected layer of corrosion products arises more rapidly.

X-ray diffraction study established that in the absence of corrosion-active gases, the corrosion products consist cheifly of Tl_2O, TlOH, Tl_2O_3, and TlOOH, with traces of Tl_2CO_3. In the presence of hydrogen sulfide, sulfides of uni- and trivalent thallium are detected in substantial amounts. The composition of the corrosion products in the presence of SO_2 has not been entirely determined.

In [1] the following reaction was proposed as the basis of the mechanism of the corrosion of thallium at low relative humidities (< 30%):

$$2Tl + H_2O = Tl_2O + H_2 \text{ (gas)}. \quad (1)$$

However, at 25° the calculated change in the free energy, according to the data of [6], comprises $\Delta F = 24.2$ kcal/mole for liquid water and $\Delta F = 22.1$ kcal/mole for water vapor. At the same time, for the oxidation of thallium by oxygen, $\Delta F = -32.5$ kcal/mole [6]. Thus, from the thermodynamic standpoint the oxidation by oxygen is preferable.

The high overvoltage of hydrogen on thallium [7] and the strong dependence of the rate of corrosion of thallium in aqueous solutions on the oxygen concentration [2, 8] permit us to conclude that atmospheric corrosion under a film of moisture (formed on thallium at moisture contents above 30%) proceeds with oxygen depolarization:

$$O_2 + 2H_2O + 2\bar{e} \rightarrow H_2O_2 + OH^- \quad (2)$$
$$H_2O_2 + 2\bar{e} \longrightarrow 2OH^- \quad (3)$$

Since regardless of the presence of H_2O_2 in aqueous solutions, only univalent ions are formed in the electrochemical dissolution of thallium [9], the anodic process during atmospheric corrosion can be represented by the equation

$$Tl - \bar{e} \longrightarrow Tl^+ \quad (4)$$

As a result of secondary chemical reactions, compounds of univalent thallium (TlOH, Tl_2CO_3, etc.) are formed. Compounds of trivalent thallium are detected only after considerable time intervals, possibly as a result of the oxidation of Tl^+ by hydrogen peroxide. With increasing temperature the fraction of Tl^{3+} in the corrosion products increases, but it does not depend on the relative air humidity within the limits of the experimental error (Table 2). Since oxygen compounds of trivalent thallium may be soluble in water [10], their appearance may explain the deviation of the kinetic curve from a linear function, observed at high temperatures.

The apparent order of the oxidation of thallium with respect to water, according to our data, is $dv_k/dpH_2O = 0.25$ instead of two, which is required according to the mechanism of Weber and Sturdy [1].

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