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Abstract

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ON THE RELATION BETWEEN THE EVOLVED H_2O_2 AND THE NUMBER OF OXIDE MOLECULES FORMED DURING ATMOSPHERIC CORROSION OF Mg AND Al

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The photographic method for investigating the atmospheric corrosion of metals is based on the fact that the hydrogen peroxide formed during oxidation is capable of producing a latent photographic image. Owing to the developed method for increasing the sensitivity of the photographic layer to the action of H_2O_2 vapors, it is possible to study the corrosion of metals at very early stages (fractions of a second from the onset of oxidation ([1])). In this respect, as well as in its simplicity, the photographic method of investigation has an advantage over other known methods. To substantiate it, it is necessary to show that the H_2O_2 formed during oxidation of metals is one of the principal links of the corrosion process ([2]). Evidence of this could be provided by agreement between the results of investigating the kinetics of atmospheric corrosion by the photographic method and by some other method, theoretically and experimentally substantiated. As the method for comparison, the optical polarization method for studying thin films was chosen; it was theoretically developed by Drude ([3]) and widely applied experimentally and refined by Tronstad and Winterbottom ([4]) for investigating metal corrosion. This method is based on the study of the parameters of elliptic polarization of light (Δ and ψ), reflected from a metal surface, which change during oxidation and depend on the optical properties of the metal and the thickness of the oxide film on its surface. These parameters are related to the thickness of the oxide film and its refractive index by the following dependences:

$$L = \frac{\Delta - \overline{\Delta}}{A\left(1 - \frac{1}{n_1^2}\right)}; \qquad n_1^2 = \frac{1 + \frac{2\psi - 2\overline{\psi}}{\Delta - \overline{\Delta}} \cdot \frac{\cos^2\varphi - a}{a' \sin 2\psi}}{\cos^2\varphi}, \tag{1}$$

where

$$A = -\frac{4\pi}{\lambda}\frac{\cos\varphi\,\sin^2\varphi\,(\cos^2\varphi - a)}{(\cos^2\varphi - a)^2 + a'^2}; \qquad a = \frac{1-x^2}{n^2(1+x^2)^2}, \qquad a' = \frac{2x}{n^2(1+x^2)^2},$$

L is the layer thickness, n_1 is the refractive index of the layer, λ is the wavelength of the incident monochromatic light, n is the refractive index of the metal, x is the absorption coefficient of the metal, φ is the angle of incidence of the ray on the metallic surface, and ψ is the angle of inclination of the plane of oscillation of the incident linearly polarized light to the plane of incidence, characterizing the relative change in the amplitudes of the components lying in the plane of incidence and perpendicular to it for the reflected light.

Upon reflection, not only the amplitudes of the components change, but also their phases. If $\delta_\parallel$ and $\delta_\perp$ are the phases of these components after reflection, then $\delta_\parallel - \delta_\perp = \Delta$. The bars over $\overline{\Delta}$ and $\overline{\psi}$ mean that these parameters are determined for a clean metallic surface, while Δ and ψ without bars denote the parameters

in the presence of an oxide film. The optical constants of the metal are expressed through $\overline{\Delta}$ and $\overline{\psi}$, approximately, as follows:

$$n = \frac{\sin\varphi\ \mathrm{tg}\,\varphi\cos 2\overline{\psi}}{1+\cos\overline{\Delta}\sin 2\overline{\psi}}, \qquad \chi = \sin\overline{\Delta}\ \mathrm{tg}\,2\overline{\psi}. \tag{2}$$

The experimental method requires that the conditions of reflection from the metal surface be identical over the entire area on which the rays fall, i.e., there must be one and the same plane of incidence and angle of incidence. For this purpose, the Mg and Al specimens were subjected to fine grinding with GOI pastes. The height of the irregularities of the profile of the metallic surface lay within grades 10-11 ($H_{\text{sk}} = 0.14$—$0.1\,\mu$). The prepared specimen was placed on the table of a polarization goniometer constructed in our laboratory,* after which the initial values of $\overline{\Delta}$ and $2\overline{\psi}$ were recorded for the clean metallic surface. From $\overline{\Delta}$ and $2\overline{\psi}$, on the basis of formulas (2), the constants n and χ for the metal were calculated. Then, as an oxide layer formed on the metal surface, the values of Δ and 2ψ were measured. From these values, using formulas (1), L and n_1 of the oxide layer on the metal were determined at various times after the start of oxidation. The use of an SVD-120A lamp with a brightness of about 5000 stilbs, careful adaptation of the eye (15 min), and strict maintenance of the immobility of the specimen on the object table throughout the entire process of studying the kinetics (5 h) made it possible to measure L to within 2—3 Å. For n, χ, and n_1 the following data were obtained: at $\lambda = 5890$ Å and $\varphi = 60°$, for Al $n = 2.37$; $\chi = 1.53$; $n_1 = 1.51$; for Mg $n = 0.484$; $\chi = 6.93$; $n_1 = 1.7$. The measurement results make it possible to construct curves for the kinetics of oxide growth on Mg and Al, which are presented in Fig. 1.

Fig. 1. Kinetic curves of oxidation of Mg and Al, obtained by photographic and optical methods. *a* —optical method, *b* —photographic method

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The investigations were carried out at $20 \pm 1^\circ$ and relative humidity $r = 63 \pm 5\%$. Each point on the graph is the mean value of ten measurements for Al and eight for Mg.

It should be borne in mind that in all cases at the beginning of the investigation the metal surface was never sufficiently free of an oxide layer ([5]). In addition, optical investigations have shown ([6]) that on all oxidizing metals there also occurs the formation of a surface-adsorbed gas film, which, for example, reaches 9 Å for Al. If one proceeds from these data, the total thickness of the initial film should lead to a change in $\overline{\Delta}$ and $2\overline{\psi}$ for Al, respectively, by 1—1.5° and 10′—12′. Such a change in $\overline{\Delta}$ and $2\overline{\psi}$, taken as the initial values for the pure metal, has little effect on the change in n and χ calculated by formulas (2). In calculations of L this gives an error of about 2-3%.

Hence the increase in oxide-film thickness on Mg and Al shown in the graphs may be regarded as quite reliable. Determinations of the oxide thickness on Al after 24 h gave values $L = 17$—20 Å. Subsequently, with the passage of time, the growth of the oxide film slowed down considerably, and after 24 h L increased by less than 4 Å. On Mg, even after 2-3 days an increase in oxide thickness was observed: $L_{24\,\mathrm{h}} \sim 15$ Å; $L_{48\,\mathrm{h}} \sim 22$ Å.

Straightening the curves in Fig. 1 gives the following regularities of growth of L

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* We take this opportunity to express our gratitude to V. A. Marchenko, who with great care performed the mechanical part of the polarization goniometer.

in the time interval studied (5 h): for Al $L^2 = 31t$; for Mg $L^{2.69} = 63t$. Under the same conditions of temperature, humidity, and specimen preparation, the oxidation kinetics of Mg and Al were studied by the photographic method.

Chemical composition of the metals studied (impurities in %):

	Fe	Si	Mg	Cu
Mg	0.004	0.009	0.0021	–
Al	0.0016	0.0016	–	0.001

Figure 2

Figure 2: Figure 2

Finely polished Mg and Al specimens were placed on a photographic plate and kept on it for 0.5, 1, 2, 3, 4, and 5 hours. Photometry was used to determine the optical density of the blackenings D produced as a result of the action of the H_2O_2 liberated during oxidation on the photographic layer (Fig. 2). Then the values of the optical density of the blackenings (which were averages of six experiments) were recalculated into the absolute number of liberated H_2O_2 molecules. For this:

Fig. 2. Curves of the dependence of the optical density D on the exposure time of Mg and Al on the photographic plate and on the number of liberated H_2O_2 molecules falling on the photographic layer

1. The dependence between the density of blackening D and the concentration of an H_2O_2 solution producing this blackening was established.
2. The amount v of evaporated H_2O_2 solution under the experimental conditions was determined (above the surface of the evaporating solution, for 1 min, at a distance of 2 mm the photographic plate was placed, with the emulsion facing the solution, at $20 \pm 1^\circ$ and at $r = 63 \pm 5\%$). It was found that $v = 0.218$ mg/cm$^2 \cdot$ min, constant for the concentration of H_2O_2 solution in the range studied, 0.05–2%.
3. The mole fraction of H_2O_2, y_h, in the vapors above a hydrogen peroxide solution of specified concentration was calculated by the formula of Skatchard et al. ([7]). Knowing v and y_h, one can calculate the number $n'_{H_2O_2}$ of H_2O_2 molecules producing this blackening, since there is a direct relationship between the numbers of H_2O_2 molecules liberated and reaching the photographic layer ([1]):

$$n'_{H_2O_2} = vy_hN/M_h \tag{3}$$

(N is Avogadro' s number, M_h is the molecular weight of the H_2O_2 solution). But since the photographic plate is located at a distance of 2 mm from the surface of the solution, and $n'_{H_2O_2}$ decreases exponentially with height ([8]), then

$$n'_{H_2O_2} = n^0_{H_2O_2} e^{-0.417 \cdot 2} \tag{4}$$

will be the number of H_2O_2 molecules which, being liberated from 1 cm^2 of the surface of the solution, produces this blackening on 1 cm^2 of the visible surface of the photographic plate, if it is located directly at the solution. From the values of $n'_{H_2O_2}$ calculated in this way, a calibration graph $D = D(n')$ was

constructed (Fig. 2). Using this graph, one can proceed to the kinetics of H_2O_2 liberation during the oxidation of Mg and Al (Fig. 1).

The coincidence of the kinetic curves of oxidation of Mg and Al in the indicated time interval, obtained by the photographic and optical methods, indicates the existence of a linear dependence between the number of liberated H_2O_2 molecules and the thickness of the oxide film. This makes it possible to conclude that a strictly definite number of H_2O_2 molecules formed corresponds to the elementary act of formation of an oxide molecule. Consequently, the H_2O_2 liberated during oxidation can serve as a criterion for studying the corrosion process on a metal.

It was further ascertained what the ratio is between the number of evolved H_2O_2 molecules and the number of molecules of the oxides MgO and Al_2O_3. To calculate the absolute number of oxide molecules corresponding to the number of evolved H_2O_2 molecules, it is necessary to know the true surface area of the oxidizing specimen. In order to determine the effect of the grinding grade on the true surface area of the metals, special studies were carried out on a profilograph–profilometer of the "Kalibr–VEI" type (the vertical magnification when recording surface profilograms can be varied from 2000 to 120000 times, and the horizontal magnification from 117 to 4200 times). The length of the curve of the profile of the metal surface with different treatment was determined, taking into account the vertical and horizontal magnifications, which were selected for each grinding case. Comparison of the length of the curve of the surface profile with the corresponding straight line makes it possible to judge the magnitude of the true surface area of the metal in comparison with the geometric one. As a result it was established that profile irregularities within the range 0.01–2 μ cause an increase of the geometric surface by no more than 3%. On the basis of experiments measuring the amount of ions adsorbed on metals, Erbacher ([9]) came to the conclusion that the true surface area of metals, irrespective of the type of grinding, is 2.5 times greater than the geometric area. A comparison of our data with Erbacher' s data makes it possible to conclude that the difference between the geometric surface area of metals and the true area is caused by irregularities lying beyond the limits of the highest class of metal treatment. Taking into account a roughness coefficient equal to 2.5, we obtain the following ratios between the number of evolved H_2O_2 molecules during oxidation and the corresponding number of oxide molecules:

$$1H_2O_2 \text{ — } 11.5\,Al_2O_3,$$

$$1H_2O_2 \text{ — } 27.5\,MgO. \tag{5}$$

Let us give an example of the calculation of the ratios (5). With a two-hour exposure on the photographic plate, Mg gives a blackening $D = 1.51$. This D corresponds to

$$n'_{H_2O_2} = 3.15 \cdot 10^{14},$$

which represents the number of molecules evolved from 1 cm^2 of the visible surface of the metal (formulas (3) and (4) and Fig. 2). If the roughness coefficient 2.5 is taken into account, then 1 cm^2 of the visible surface of the photographic plate corresponds to $(2.5 \cdot 1)$ cm^2 of true metal surface. In the volume of oxide V formed on Mg under this surface in 2 hours, there is a number of molecules n'_{MgO} equal to:

$$n'_{MgO} = \frac{(2.5 \cdot 1)\ cm^2 \cdot L \cdot 10^{-8}\ cm \cdot d\ g/cm^3 \cdot N\ 1/mole}{M_{MgO}\ g/mole} = 85.3 \cdot 10^{14}.$$

Thus, for Mg, the number of evolved molecules $n'_{H_2O_2} = 3.14 \cdot 10^{14}$ corresponds to $n'_{MgO} = 85.3 \cdot 10^{14}$, or $1H_2O_2$—27.2 MgO. Having performed similar calculations for all experimental values of D and L and averaging, we obtain (5). If the results of work ([2]) are taken into account, in which the authors came to the conclusion that the formation of one H_2O_2 molecule corresponds to one oxide molecule, then from ratio (5) one may conclude that a considerable fraction of the hydrogen peroxide decomposes on the surface of the metals.

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Note: Figure translations are in progress. See original paper for figures.