ATMOSPHERIC CORROSION OF METALS UNDER THE ACTION OF RADIATION

1958

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

A. V. Byalobzheskii

ATMOSPHERIC CORROSION OF METALS UNDER THE ACTION OF RADIATION

(Presented by Academician A. N. Frumkin, 16 X 1957)

Up to the present time no works have been published devoted to the study of the action of radiation on the atmospheric corrosion of metals. Allen ([1]) points out that corrosion in gases in the presence of ionizing radiation has never been the subject of investigation, and cites the well-known fact of the absence of corrosion of the exit windows of cathode-ray tubes and cyclotrons, despite the powerful flux of radiation passing through them. This fact would seem to indicate that radiation does not exert any appreciable influence on the corrosion of metals under atmospheric conditions. Our investigations have shown, however, that in a number of cases ionizing radiation noticeably accelerates corrosion processes in the atmosphere.

The investigations were carried out in a closed glass vessel at 98% relative humidity. The radiation sources used were an electron tube, a BFV-70 X-ray tube, and a Co^{60} preparation.

Table 1

Effect of radiation on the corrosion of various metals in an air atmosphere at 98% relative humidity (irradiation duration 16 hours, temperature 25°)

Source of radiation	Irradiated metal	Appearance of specimen after irradiation	Weight gain, g/specimen
Electron tube, 800 kV, 4.1 μA	Iron	Covered with continuous reddish-brown corrosion products	0.0247
Same	Copper	Along the edge, an olive-colored rim; in the center, brick-red corrosion products	0.0120

Source of radiation	Irradiated metal	Appearance of specimen after irradiation	Weight gain, g/specimen
» »	Aluminum	Separate whitish corrosion spots	0.0023
» »	Steel IX18N9T	Shiny, without visible traces of corrosion	0
Electron tube, 4.1 μA, 400 kV	Zinc	Covered with whitish corrosion products	0.0053

Notes. 1. For all the metals tested, control corrosion experiments were carried out in parallel under the same conditions, but without irradiation. In all cases the metals retained their original appearance and had no weight changes. 2. For the iron specimen, the corrosion rate was calculated and proved to be equal to 1 mm/year.

It was established (see Table 1) that the corrosion of iron, copper, and zinc—and, to a noticeably lesser extent, aluminum—is sharply accelerated under the action of ionizing radiation in a humid atmosphere (the metals are listed in order of decreasing effectiveness of the action of radiation). In our experiments, no intensifying effect of radiation on the corrosion of stainless steel was observed at all. Consequently, under atmospheric conditions the action of radiation is least effective with respect to metals capable of forming strong oxide films on their surface.

Figure 1 shows photographs of iron specimens after irradiation. For comparison, a photograph is given of a specimen that was not irradiated.

It was also established that in a dry atmosphere (drying with phosphorus anhydride) corrosion does not occur under any irradiation conditions. This indicates that, under irradiation in atmospheric conditions, corrosion proceeds beneath a moist film formed on the metal surface as a result of condensation or adsorption of water vapor on it and, consequently, is electrochemical in character, like ordinary atmospheric corrosion. The data of Table 2 show that increasing the intensity of irradiation increases the corrosion rate of iron.

Table 2

Influence of radiation intensity on the corrosion of Armco iron in an atmosphere at 98% relative humidity (irradiation duration 10 h, temperature 25°)

Radiation source	Current, μA	Position of specimen in apparatus	Absorbed energy, eV/cm^3 sec	Weight gain of specimen, g
Electron tube	4.1	Top	$1.9 \cdot 10^{19}$	0
Electron tube	4.1	Bottom	$6.8 \cdot 10^{17}$	0.0133
Electron tube	1.0	Top	$4.7 \cdot 10^{18}$	0.0060
Electron tube	1.0	Bottom	$1.7 \cdot 10^{17}$	0.0061
Electron tube	0.4	Top	$1.9 \cdot 10^{18}$	0.0043
Electron tube	0.4	Bottom	$6.8 \cdot 10^{16}$	0.0021
X-ray tube BFV-70, 50 kV	200	Top	$2.7 \cdot 10^{18}$	0.0050
X-ray tube BFV-70, 50 kV	200	Bottom	$5.3 \cdot 10^{16}$	0.0018
X-ray tube BFV-70, 50 kV	50	Top	$6.8 \cdot 10^{17}$	0.0006
X-ray tube BFV-70, 50 kV	50	Bottom	$1.3 \cdot 10^{16}$	0

The unexpected, at first glance, fact that the upper specimen, irradiated by an electron current of 4.1 μA and having absorbed the maximum amount of energy, did not corrode at all is, as our investigations showed, the result of the action of a secondary factor—the heating of the specimen as a result of absorption of a large amount of energy, which leads to the removal from the metal surface of the moisture film necessary for the corrosion process to proceed in the atmosphere, as indicated above. Cooling the upper specimen with water or air immediately led to intense corrosion of its irradiated surface. The intensifying action of radiation is very clearly seen from the experiments presented in Figs. 2 and 3: in both cases the metal, protected from direct incidence of radiation, does not corrode at all.

The intensification of the corrosion process under irradiation may be the result of a change either in the state of the corrosive medium or in the state of the surface layer of the metal. To resolve this question, we performed the following experiment: two specimens were placed with a 5-mm lead gasket between them.

In the upper of these specimens, $2.8 \cdot 10^{16}$ eV/sec was absorbed. In the lower, the amount of absorbed energy was zero (if the negligible influence of scattered radiation is not taken into account). Despite this difference, both specimens corroded identically. This shows that the principal role in enhancing corrosion under irradiation is played by the products of radiation-induced change in the atmosphere, and not by activation of the metal surface.

We set up a series of experiments to clarify the role of the main components of the atmosphere—oxygen and nitrogen; the results are given in Table 3.

The data presented show that nitrogen, inert under ordinary conditions, becomes corrosion-active in the presence of radiation. Activation of nitrogen occurs only in the presence of oxygen and, consequently,

Fig. 1. Photographs of iron specimens after corrosion tests in an atmosphere of 98% relative humidity. **A**—without irradiation (10 hr); **B** and **V**—after X-ray irradiation (10 hr); **G**—after irradiation with a $3\mu a$ electron beam (15 hr); **D**—after irradiation with a cobalt source (70 hr). **A** and **B**—2×; **V**, **G**, and **D**—30×.

Fig. 3. Effect of the direct action of an X-ray beam (**A**) and electron irradiation (**B**) on the corrosion of an iron specimen. **A1**—unprotected specimen, 2×; **A2**—specimen behind a 5-millimeter lead partition, 2×; **B**—area exposed on the right, protected by lead on the left.

must be attributed to the formation of its oxygen products, the most important of which is N_2O_5.

V. G. Khlopin established as early as 1911 that, under the action of ultraviolet rays in moist air, ozone, hydrogen peroxide, and nitric anhydride are formed ([2]). The analyses we carried out of the atmosphere in the working vessel after irradiation showed that the greatest amount of ozone (with electron irradiation 4.1 μa, 800 kV) was 0.4% in air and 0.5% in pure oxygen. The amount of nitrogen oxides, calculated as NO_3', was about 0.08%. Hydrogen peroxide was not detected quantitatively by us. Evidently it was formed in negligible amounts. All these long-lived products of irradiation of the atmosphere undoubtedly exert an intensifying effect on corrosion processes. The short-lived products of radiation action (OH and OH_2 radicals, O atoms, compounds of the type NO_3, etc.) act even more actively, as is shown by the experiments presented in Figs. 2 and 3.

Table 3

Corrosion of Armco iron in 10 h in various gas mixtures at 98% relative humidity and irradiation on an electron tube (2.0 μa; 800 kV)

Fig. 2. Schemes of experiments on the influence of the direct action of an X-ray beam (A) and electron irradiation (B) on corrosion of an iron specimen. Scheme A: 1 —unprotected specimen, 2 —specimen protected by a 5-millimeter lead partition, 3 —Scheme B: 1 —specimen; 2 —lead half-disk 5 mm thick

Figure 1: Fig. 2. Schemes of experiments on the influence of the direct action of an X-ray beam (A) and electron irradiation (B) on corrosion of an iron specimen. Scheme A: 1 —unprotected specimen, 2 —specimen protected by a 5-millimeter lead partition, 3 —Scheme B: 1 —specimen; 2 —lead half-disk 5 mm thick

Atmosphere	Upper specimen, energy absorbed $0.8 \cdot 10^{19}$ eV/cm^3 • s; weight gain in g/specimen	Lower specimen, energy absorbed $3 \cdot 10^{17}$ eV/cm^3 • s; weight gain in g/specimen
Pure oxygen	0.0031	0.0019
Nitrogen 80%, oxygen 20%	0.0059	0.0079
Argon 80%, oxygen 20%	0.0010	0.0024
Pure nitrogen	0.0001	0.0002

It is interesting that the magnitude of corrosion in pure oxygen does not increase noticeably in comparison with the argon-oxygen mixture. Evidently, this is the result of the passivating action of the strongly oxidizing medium created in oxygen upon irradiation.

Fig. 2. Schemes of experiments on the influence of the direct action of an X-ray beam (A) and electron irradiation (B) on corrosion of an iron specimen. Scheme A: 1 —unprotected specimen, 2 —specimen protected by a 5-millimeter lead partition, 3 —Scheme B: 1 —specimen; 2 —lead half-disk 5 mm thick

According to our assumptions, the intensification by radiation of the process of atmospheric corrosion is explained by the fact that the radiation products formed strengthen the corrosion current of microcouples, acting as energetic cathodic depolarizers. The indicated assumption is currently being tested experimentally by us.

In conclusion I express my gratitude to Prof. N. D. Tomashov for a number of valuable suggestions in discussing the present work.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
11 X 1957

REFERENCES

1. A. Allen, in: *Scientific and Technical Foundations of Nuclear Power Engineering*, ed. by K. Goodman, 2, IL, 1950, p. 224.

2. V. G. Khlopin, *ZhRFKhO*, 43, 554 (1911).

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