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I. L. Roikh, L. N. Koltunova, V. E. Tolkachev, V. P. Kirichenko

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Abstract

Full Text

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I. L. Roikh, L. N. Koltunova, V. E. Tolkachev, V. P. Kirichenko

STUDY OF THE ATMOSPHERIC CORROSION OF VACUUM CONDENSATES OF VARIABLE COMPOSITION IN THE Mg–Zn SYSTEM

(Presented by Academician S. A. Vekshinsky, 5 VI 1964)

Atmospheric corrosion of alloys of the Mg–Zn system was studied by combining two rapid methods: the method for obtaining alloys of variable composition proposed by Academician S. A. Vekshinsky ([1]), and a photographic method for studying atmospheric corrosion developed in our laboratory.

Previously it was shown that hydrogen peroxide released during oxidation of metals, which causes blackening of a photographic plate, can serve as a criterion of atmospheric corrosion of metals ([2,3]).

Alloys of variable composition of the Mg–Zn system were obtained by simultaneous evaporation of the metals under vacuum conditions of $5 \cdot 10^{-5}$ mm Hg from two cylindrical crucibles, followed by condensation on a glass substrate.

Fig. 1. Corrosion diagram of freshly prepared vacuum condensates of alloys of the Mg–Zn system

The composition of the alloys at any point of the sample obtained was determined from the distribution of the pure components condensed under the same conditions as the alloy of variable composition ([1]). Since at the beginning of heating the necessary evaporation regime is not yet established, the substrate had to be protected by a special screen, which was moved aside when complete stability of the thermal regime had been reached. The temperature of the cru-

Fig. 2. Corrosion diagrams of Mg—Zn alloys. 1 —naturally aged condensates, 2 —annealed condensates, 3 —unannealed massive alloys, 4 —annealed massive alloys

Figure 2: Fig. 2. Corrosion diagrams of Mg—Zn alloys. 1 —naturally aged condensates, 2 —annealed condensates, 3 —unannealed massive alloys, 4 —annealed massive alloys

cibles was controlled during deposition, which in our experiments lasted 150 min, and remained constant to within ±5°.

The temperature of the substrate before the start of condensation was 50°; the thickness of the vacuum condensates was several tens of microns. After air was admitted, the surface of the condensate was cleaned with micron-grade emery paper, and then corrosion tests were carried out under atmospheric conditions at 20°C and a relative humidity of 65-70%. For this purpose, after being held in air for 15 min, the vacuum condensate was placed on a specially treated purchased photographic plate. Preliminary treatment of the photographic plate was carried out in order to increase the sensitivity of the emulsion to the action of hydrogen peroxide ([4]).

The blackening of the photographic plate, other conditions being equal, depends on the corrosive properties of the alloy that caused the given blackening. From the blackening, the number of hydrogen peroxide molecules released during atmospheric corrosion was determined ([5]).

On the basis of the photographic experiments a corrosion diagram was constructed: the number of H_2O_2 molecules versus the composition of the Mg—Zn system (Fig. 1). Along the ordinate is plotted the number of H_2O_2 molecules released over 24 hours of the oxidation process of freshly prepared vacuum condensates of Mg—Zn.

A relationship was established between the corrosion properties and the phase diagram of alloys of the Mg—Zn system: a corrosion minimum is characteristic for alloys whose composition is close to the eutectic point (50-60% Zn); the lowest corrosion resistance corresponds to the intermetallic compound $MgZn_2$.

To substantiate the possibility of extending the results of corrosion tests of vacuum condensates to massive alloys, the corrosion properties of massive specimens of the Mg—Zn system were studied. The alloys were obtained by melting under a flux (60% LiCl and 40% KCl). The results of experiments carried out with massive alloys are presented in Fig. 2 ([3,4]), from which it is seen that the course of the corrosion diagram for massive specimens generally corresponds to the corrosion diagram of vacuum condensates of alloys.

Fig. 2. Corrosion diagrams of Mg—Zn alloys. 1 —naturally aged condensates, 2 —annealed condensates, 3 —unannealed massive alloys, 4 —annealed massive alloys.

The greater corrosion activity of freshly prepared vacuum condensates in comparison with massive alloys is apparently explained by the nonequilibrium and disordered structure of the vacuum condensates, their more developed surface, and also by the presence of micropores in which capillary condensation of moisture occurs. Obviously, bringing vacuum condensates into a state close to equilibrium should have a substantial effect on the corrosion behavior of vacuum condensates of alloys.

In this connection, the influence of natural aging (storage for 3 months at room temperature) and artificial aging (annealing at 200° for 3 days) on the corrosion properties of vacuum condensates of Mg—Zn alloys was studied. It was established that the aging process leads to an improvement in their corrosion properties, manifested in an increase in the protective action of oxide films formed on the surface of the indicated alloys during atmospheric corrosion.

From Fig. 2 ([1,2]) it follows that natural aging proves more effective than annealing for vacuum condensates of alloys containing more than 70% Zn. Comparison of the corrosion diagrams (Fig. 2) makes it possible to conclude that, in terms of the nature of the influence of annealing on the corrosion properties of alloys of the Mg—Zn system, there is a direct relationship between vacuum condensates and massive alloys: in both cases annealing proves most effective for alloys containing less than 70% Zn.

Since in the Mg—Zn system the composition 50-60% Zn is the most corrosion-resistant under atmospheric conditions, we carried out a more detailed investigation of vacuum condensates in this concentration range, as well as of the pure components. The kinetics of atmospheric corrosion during the first two hours of the oxidation process was studied by photographic and, in parallel, optical-polarization methods. The results are given in Fig. 3.

The laws governing the growth of oxide-film thickness and the liberation of hydrogen peroxide during atmospheric corrosion of vacuum condensates of Mg, Zn, and an alloy (50-60% Zn) were established:

$$\begin{array}{lll} \text{Magnesium} & L = 0.35t + 9, & n = 0.17 \cdot 10^{14}t + 1.2 \cdot 10^{14}, \\ \text{Zinc} & L = 0.19t + 1.5, & n = 0.073 \cdot 10^{14}t + 0.6 \cdot 10^{14}, \\ \text{Alloy} & L^{1.5} = 0.33t, & n^{1.5} = 2.35 \cdot 10^{19}t. \end{array}$$

Here L is the thickness of the oxide layer, in Å; n is the number of H_2O_2 molecules released from 1 cm^2 of the visible surface of the condensate; t is time in minutes, with 15 min $\leq t \leq$ 120 min.

The observed agreement in the character of the dependence of H_2O_2 evolution and of the increase in the thickness of the oxide layer on oxidation time indicates the possibility of judging the corrosion behavior of metals and alloys on the basis of photographic experiments.

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

Fig. 3. Kinetics of atmospheric corrosion of vacuum condensates: **1** –magnesium, **2** –zinc, **3** –alloy with 50-60% Zn. **a** –kinetics of growth of the oxide-layer thickness, **b** –kinetics of H_2O_2 evolution.

Along with the corrosion investigations, measurements of the microhardness H_μ were carried out. In Fig. 4 a microhardness-composition diagram is presented for vacuum condensates and massive alloys of the Mg–Zn system. The microhardness was measured under a load of 50 g.

Fig. 4. Microhardness-composition diagram of the Mg–Zn system: **a** –vacuum condensates, **b** –massive alloys.

The character of the dependence of H_μ on composition for vacuum condensates generally corresponds to the microhardness-composition diagram for massive alloys of the Mg–Zn system. The maximum microhardness corresponds to the intermetallic compound $MgZn_2$. An alloy containing 50-60% zinc is not inferior to zinc in its corrosion properties and at the same time is lighter (specific gravity ~ 2.8 g/cm^3) and has a significantly greater microhardness (on average by a factor of 7).

In conclusion, we note that the combination of the method for obtaining alloys of variable composition and the photographic method for studying atmospheric corrosion makes it possible to determine the corrosion properties of the selected system of metals over the entire concentration range in a comparatively short time.

Odessa Technological Institute
named after M. V. Lomonosov

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