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Rate of Formation of Film on Metals and Alloys

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The rate of atmospheric corrosion of Cu−Zn and Cu−Mg alloys are retarded by Al or Mn, and the law of the growth of film in the case of Cu−Zn alloys changes over from the parabolic to the logarithmic law on the addition of Al or Mn. For Cu−Mg alloys under a given set of conditions the law of the growth of film is governed by

$$x^{\frac{1}{2}} = k_1 \log t + k_2,$$

where x is the film thickness, t is time, and k_1 and k_2 are constants. It has been indicated that some experimental data on the corrosion of metals and alloys may be quantitatively represented if two or more functions, representing different mechanisms of the growth of film, are taken into consideration simultaneously.

INTRODUCTION

An attempt has been made in this paper to study the laws of the growth of films on some copper-zinc and copper-magnesium alloys with or without the addition of aluminum or manganese under different humidity conditions at atmospheric temperature and to show that the experimental data may not only be qualitatively explained but represented quantitatively, if two or more functions, representing different mechanisms of the growth of the film, are taken into consideration simultaneously.

EXPERIMENTAL PROCEDURE

The alloys were carefully prepared in an electrical resistance furnace and cast into small ingots. Test pieces in the form of cylinders (25 to 30 mm long and 5 to 10 mm in diameter) were annealed under vacuum at 200°C for 8 hours. The samples were exposed to air in a vessel for different periods of time at known temperature, pressure, and humidity conditions. The film thickness was measured accurately before and after atmospheric corrosion at known magnifications (100× to 450×).

EXPERIMENTAL RESULTS AND DISCUSSIONS

The experimental results are given in Tables I, II, and III and plotted in Figs. 1, 2, and 3. It may be noted from Fig. 1 that with 65 percent humidity at 22°C and 755 mm Hg pressure:

A. (a) for the Cu−Zn alloy, the film thickness x as function of $t^{\frac{1}{2}}$ is linear, and hence it obeys the parabolic law of growth of film;
(b) for the Cu−Zn−Mn alloy, however, x as function of $t^{\frac{1}{2}}$ is not linear, but x as function of $\log t$ is linear (curve I, Fig. 1). Thus the growth of the film obeys the logarithmic law;
(c) the film on the Cu−Zn−Al alloy also obeys the logarithmic law (curve II, Fig. 1);

B. (a) for the Cu−Mg alloy, x is neither a parabolic nor a logarithmic function of t (it will be explained later that $\sqrt{x}$ is a linear function of $\log t$ for this alloy);
(b) for the Cu−Mg−Mn alloy, x is a logarithmic function of t;
(c) for the Cu−Mg−Al alloy also x is a logarithmic function of t.

Thus the effects of Mn and Al tend to change the rate of growth of films on Cu−Zn alloys from the parabolic to the logarithmic law. It is not unlikely that the lower conductivities of oxides of manganese and the comparatively higher strength of Al_2O_3 are primarily responsible for such changes.

TABLE I. The composition of the alloys.

Alloys	Cu	Zn	Mg	Mn	Al
Cu−Zn	60.28	39.70	···	···	···
Cu−Zn−Mn	58.70	39.12	···	2.10	···
Cu−Zn−Al	59.10	39.83	···	···	1.00
Cu−Mg	77.0	···	23.0	···	···
Cu−Mg−Mn	70.0	···	28.0	1.96	···
Cu−Mg−Al	73.0	···	25.3	···	1.78

TABLE II. The film thicknesses as function of time t, for the different alloys at 220°C, 755 mm Hg pressure of air with 65 percent average humidity. Data plotted in Fig. 1.

Time t in hours	Film thickness $\times 10^4$ mm			Film thickness $\times 10^3$ mm		
	Cu−Zn	Cu−Zn −Mn	Cu−Zn −Al	Cu−Mg	Cu−Mg −Mg	Cu−Mg −Al
25 hours	84	52	60	391	191	176
50 hours	91	71	66	404	208	192
110 hours	113	90	76	428	229	206
206 hours	132	100	83	445	242	218
350 hours	156	112	88	464	253	226

TABLE III. The film thickness x as function of time t for the different alloys at 34°C, 752 mm of air saturated with moisture. Data plotted in Figs. 2 and 3.

Time t in hours	Film thickness $\times 10^3$ mm	
	Cu−Mg	Cu−Mg−Mn
25 hours	400	120
50 hours	412	140
110 hours	452	182
206 hours	580	280
350 hours	960	462

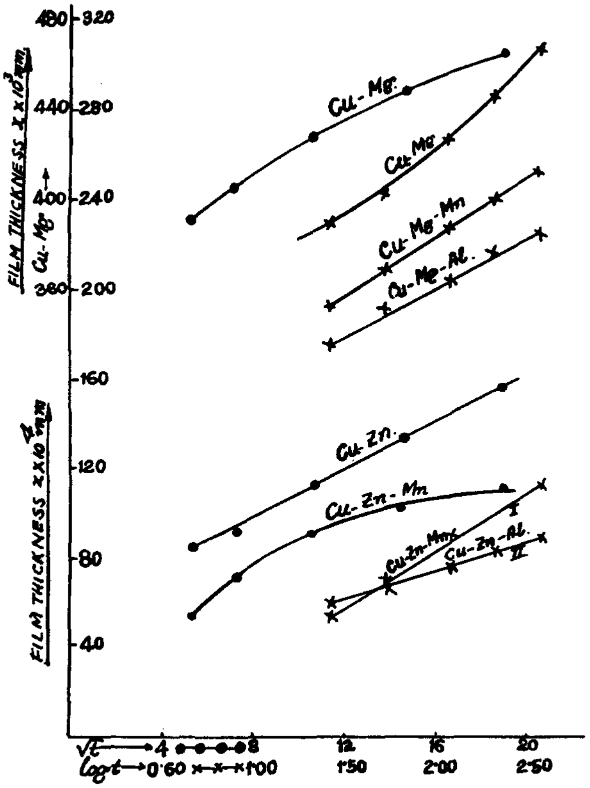

FIG. 1. Film thickness x as function of $t^{\frac{1}{2}}$ (●—●—●) and as function of $\log t$ (×—×—×) for different alloys at 22°C, 755 mm Hg pressure and 65 percent humidity.

The data in Table III plotted in Fig. 2 show that the film thickness x on Cu−Mg alloys tends to increase progressively with time when the atmosphere is saturated with moisture. It is not unlikely that in the case of Cu−Mg alloys with 100 percent humidity the growth of film tends to follow an exponential law. In connection with the atmospheric corrosion of iron, Evans[1] has pointed out that Vernon obtained similar results in an atmosphere of fairly high humidity intermittently reaching the saturation value.

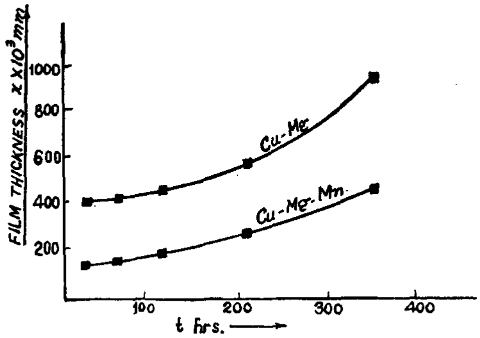

FIG. 2. Film thickness x as function of time t for Cu−Mg and Cu−Mg−Mn alloys for air saturated with moisture at 34°C, 752 mm Hg pressure.

[1] U. R. Evans, *Corrosion of Metals* (Edward Arnold and Company, London, 1926), p. 164.

In another paper[2] an equation has been derived by a combination of the parabolic and logarithmic law and the rates of formation of films on some metals and alloys have been explained on the basis of simultaneous actions of different factors. In connection with iodide films on silver, Evans and Bannister[3] have shown that x is first a linear and then a parabolic function of t. Bircumshaw and Everdell[4] obtained similar results with iodide films on copper. It is not unlikely that in one case a factor which tends to produce a linear function and another which tends to produce a parabolic function may be operative simultaneously. For example, it may be easily shown that if dx/dt be proportional to x and also proportional to $e^{-cx^{\frac{1}{2}}}$ one gets on integration

$$x^{\frac{1}{2}}=k_1 \log t+k_2.$$

In other words, $x^{\frac{1}{2}}$ is a linear function of $\log t$. How far this is true may be seen from Fig. 3 where the value of

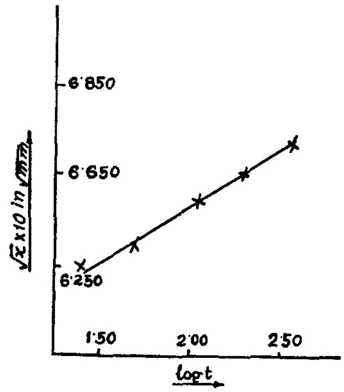

FIG. 3. $\sqrt{x}$ as function of $\log t$ for Cu−Mg alloys at 22°C, 755 mm Hg pressure and 65 percent humidity.

$x^{\frac{1}{2}}$ for Cu−Mg alloys has been plotted as function of $\log t$. It is evident, therefore, that many experimental data on the rate of formation of films on metals and alloys may be quantitatively explained when different factors and equations are taken into consideration simultaneously.

CONCLUSIONS

1. The rate of atmospheric corrosion of Cu−Zn and Cu−Mg alloys is retarded by the addition of Al and Mn.

2. The law of growth of film in the case of Cu−Zn alloys changes over from the parabolic to the logarithmic law on the addition of Mn or Al.

3. The rate of growth of films on Cu−Mg−Mn or Cu−Mg−Al obeys the logarithmic law of the growth of film.

[2] G. P. Chatterjee, Proc. Indian Sci. Congr. **III**, 247 (1952).
[3] U. R. Evans and L. C. Bannister, Proc. Roy. Soc. (London) **A125**, 125, 375 (1929).
[4] L. L. Bircumshaw and M. H. Everdell, Proc. Roy. Soc. (London) **A183**, 598 (1942).

4. Cu−Mg alloys at 22°C, 755 mm pressure and 65 percent humidity tends to obey a law of growth of films given by

$$x^{\frac{1}{2}}=k_1 \log t+k_2,$$

where x=film thickness and t=time.

5. When the humidity approaches 100 percent, the rate of growth of films on Cu−Mg alloys progressively increases with time and within certain limits tends to obey an exponential law.

6. Many experimental data on the corrosion of metals and alloys may be explained on the basis of simultaneous actions of different factors, i.e., when two or more equations, representing different mechanisms of the growth of film, are taken into consideration simultaneously.

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Creep of Aluminum under Cyclotron Irradiation*

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The effect of cyclotron irradiation by 38-Mev alpha particles on the steady-state creep rate (*ca* 10^{-6} per second) of aluminum has been measured at beam densities up to 1.2×10^{13} particles per cm^2 per second. The data, which were taken on a 0.016-inch thick aluminum specimen for a stress range of 600 to 2500 psi and over a temperature range of 160° to 330°C, showed a slight decrease in rate (up to 19 percent) during irradiation. Since the effect is small, apparently independent of beam density, and is comparable to the usual deviations in the absence of radiation, it can be considered a null result.

I. INTRODUCTION

THE effect of radiation on creep of materials has been discussed by Nabarro,[1] Slater,[2] and Dienes.[3] In a preliminary report of the present work by Yockey, Jeppson, and Keen[4] a decrease in creep rate of aluminum of from 30 percent to 60 percent was given when beam densities as high as 2.4×10^{13} alpha particles/cm^2/sec were used. The results quoted in the present paper are to be regarded as replacing those in the preliminary report. Witzig[5] has studied the effect of deuteron bombardment of OFHC copper at fluxes of about 10^{12} deuterons per cm^2 per second. He found no effect within about twenty percent. It should be noted that for a given velocity, an alpha particle is four times as effective as a deuteron or proton in producing radiation damage.

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[1] Nabarro, *Report of a Conference on Strength of Solids* (Physical Society, London, July, 1947), p. 85.

[2] J. C. Slater, J. Appl. Phys. 22, 237 (1951).

[3] G. J. Dienes, *Annual Reviews of Nuclear Science* (Annual Review, Inc., Stanford, 1953), Vol. 2, p. 187.

[4] Yockey, Jeppson, and Keen, "Effect of cyclotron irradiation on creep of aluminum," NAA-SR-121 (1951) (unpublished).

[5] W. F. Witzig, J. Appl. Phys. 23, 1263 (1952).

II. PROCEDURE

The creep tests were made on specimens milled from 0.016-inch aluminum sheet. This thickness diminishes the nonuniformity due to the Bragg Effect as 38-Mev alphas have a range of 0.023 inch in aluminum. The gauge length was 0.5 inch; the cross section 0.040 by 0.016 inch. Spectrographic analysis of a typical specimen gave the following impurities:

1. Copper, less than 0.1 percent.
2. Silicon, less than 0.1 percent.
3. Iron, less than 0.01 percent.

After the specimen was machined, it was electrolytically polished. No other heat treatment was used.

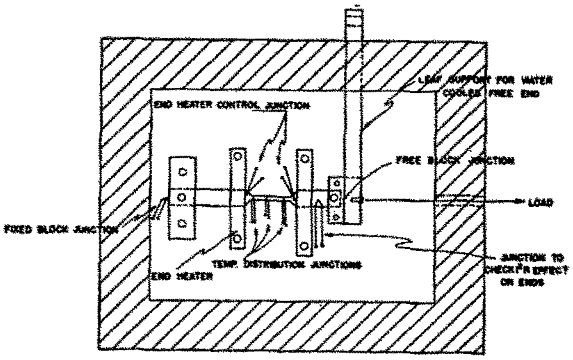

Fig. 1. Target box schematic showing placement of sample and thermocouples.