

SHORT COMMUNICATION

SPATIAL DISTRIBUTION OF PITS ON STAINLESS STEEL

R. C. SALVAREZZA*, A. J. ARVIA* and A. MILCHEV

Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria

(Received 23 January 1989)

Abstract—The spatial distribution of pits formed on a stainless steel electrode is analysed by means of two stochastic criteria based on the Poisson distribution law. Information is obtained about the character of the location of pits on the electrode surface.

The probability aspects of the pitting corrosion have been considered with increasing interest in recent years and various models have been proposed to describe some stochastic effects concerning the birth and the death of pits with time [1–6]. In this work the pitting corrosion of 316 stainless steel (SS) is studied and the spatial distribution of pits is analysed using two different criteria based on the Poisson distribution law.

The working electrodes were made of 316 SS rods mechanically polished and embedded in Araldite to expose a surface area of 0.2 cm². The counter electrode was a large platinum sheet and a saturated calomel electrode (s.c.e.) was used as reference. The electrolyte was NaH₂PO₄ + 0.05 M Na₂B₄O₇ (pH 8) + 0.5 M NaCl aqueous solution kept at 25°C. The pits (Fig. 1) were formed at a constant potential (0.80 V vs s.c.e.) as described by Salvarezza *et al.* [4, 5].

Let us assume that corrosion pits are randomly distributed on the SS surface and let us further consider that the probability (P_m) of finding the number of pits (m) in arbitrary surface elements (ΔS) is given by the Poisson equation

$$P_m = \frac{N^m \exp(-N)}{m!} \quad (1)$$

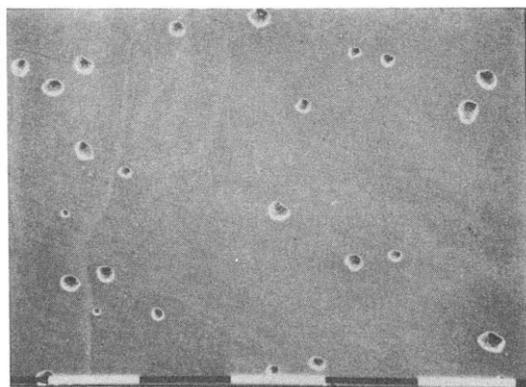


Fig. 1 Pits formed on 316 stainless steel at a constant potential 0.80 V vs s.c.e. (scale 0.1 mm)

Where N is the average number of pits in the area ΔS . In the case under consideration, P_m , the experimental probability is obtained by dividing the number of surface elements containing m pits by the total number of elements randomly located within the surface of the sample. The circles in Fig. 2 denote the experimental probabilities, P_m , and the line illustrates the theoretical distribution obtained by using Equation (1) with $N = 1.27$. This figure represents the experimentally found average number of pits corresponding to a surface element $\Delta S = 4 \times 10^{-4}$ cm². The good agreement between the theory and the experiment confirms the assumption of a random distribution of pits in the experimental system.

Another way to study the distribution of pits on the electrode surface is by analysing the distances between the nearest neighbour pits [7–9]. By definition [10], the nearest neighbour distance to a given pit satisfies the conditions (Fig. 3) (i) no pits are formed within the circle of radius r , (ii) only one pit can be formed within the annulus of width dr . By using Equation (1), for the probability of the first event ($m=0$) one obtains

$$P_0 = \exp(-\pi r^2 N_0) \quad (2)$$

where $\pi r^2 N_0$ is the average number of pits in the circle with radius r , N_0 being the pit density averaged over the total sample area. In a similar way for the probability of the second event ($m=1$) follows

$$P_1 = 2\pi r dr N_0 \exp(-2\pi r dr N_0) \approx 2\pi r dr N_0 \quad (3)$$

Then, the distribution function for the nearest neighbour distance is given by

$$Pr dr = P_0 P_1 = 2\pi r N_0 \exp(-\pi r^2 N_0) dr \quad (4)$$

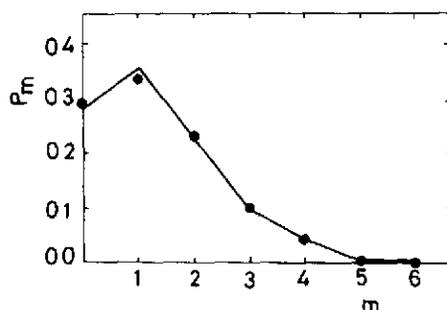


Fig. 2 Experimental (circles) and theoretical (line) probabilities of finding exactly m pits in a surface element $\Delta S = 4 \times 10^{-4}$ cm².

*Permanent address Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 1900 La Plata, Argentina

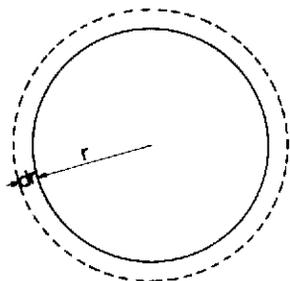


Fig. 3. Scheme for the definition of the nearest neighbour concept.

The histogram depicted in Fig. 4 shows the experimental distribution of the probability $Pr\Delta r$, ($\Delta r = 4 \times 10^{-3}$ cm), obtained by measuring the distances among nearest neighbour pits on the whole electrode surface. The line in Fig. 4 represents the theoretical curve calculated by means of Equation (4) with $N_0 = 1.98 \times 10^3 \text{ cm}^{-2}$, which is the experimental density of pits related to the geometric electrode surface area.

The second analysis seems to confirm the random distribution of pits on the stainless steel electrode. This fact leads to a relevant conclusion: the formation and subsequent growth of a single pit does not influence the appearance of other pits on the electrode surface. Indeed, if any exclusion zones arise around the growing pits the smallest distances would appear in the experimental histogram with a probability lower than that predicted by the Poisson theory. A slight effect of this kind is actually observed in Fig. 4, but at the present stage additional experiments should be carried out in order to verify if this is a systematic or a random deviation from the theoretical distribution law.

Finally, it should be noted that the location of pits on the electrode surface reflects the location of active sites for the formation of pits which for the SS specimens are assumed to be sulphide inclusions[4]. Therefore, it would be important to visualize these inclusions by an independent method and to study also their spatial distribution on the electrode surface.

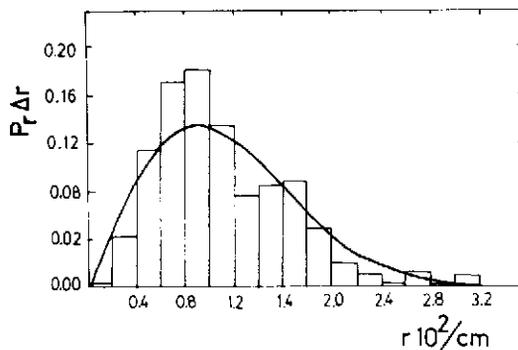


Fig. 4. Experimental (histogram) and theoretical (line) distribution of the distances among nearest neighbours.

Acknowledgement—One of us (RCS) thanks Consejo Nacional de Investigaciones Científicas y Técnicas (Argentina) and the Organization of the American States for the financial support of his visit to the Institute of Physical Chemistry, Bulgarian Academy of Sciences.

REFERENCES

1. N. Sato, *J. electrochem. Soc.* **129**, 255 (1982).
2. T. Shibata and T. Takayama, *Corrosion* **33**, 243 (1977).
3. D. E. Williams, C. Westcott and M. Fleischmann, *J. electrochem. Soc.* **132**, 1804 (1985).
4. R. C. Salvarezza, N. de Cristofaro, C. Pallotta and A. J. Arvia, *Electrochim. Acta* **32**, 1049 (1987).
5. M. Urretabizcaya, C. Pallotta, N. de Cristofaro, R. C. Salvarezza and A. J. Arvia, *Electrochim. Acta* **33**, 1645 (1988).
6. T. Shibata, Extended Abstracts, The Electrochemical Society Fall Meeting, Honolulu, Hawaii (1987).
7. A. Milchev, E. Vassileva and V. Kertov, *J. electroanal. Chem.* **107**, 323 (1980).
8. A. Milchev, *Electrochim. Acta* **28**, 947 (1983).
9. V. Platikanova and A. Milchev, *J. Imaging Sci.* **30**, 210 (1986).
10. S. Chandrasekhar, *Rev. Mod. Phys.* **15**, 1 (1943).