DISCLAIMER

STUDY OF THE CORROSION RATE BEHAVIOR OF ION IMPLANTED Fe-BASED ALLOYS

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MASTER

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ABSTRACT

We report on some studies we have made of the time evolution of the corrosion behavior of ion implanted samples of pure iron, medium carbon steel, and 18-8 Cr-Ni stainless steel. Ti, Cr, Ni, Cu, Mo and Yb were implanted at mean ion energies near 100 keV and at doses up to 1×10^{17} cm^{-2} using a Mevva metal ion implantation facility. A novel feature of this experiment was the simultaneous implantation with several different implanted species. The implanted samples were immersed in sulfuric acid solution at 40°C and the corrosion monitored as a function of time. The loss in mass was accurately measured using atomic absorption spectroscopy. The functional dependence of the corrosion behavior was established for all samples. The cumulative mass loss Q is given as a function of time t by $Q = At^N$, where A and N are parameters; thus the corrosion rate

V is given by $V = ANt^{N-1}$. A is dominated by the initial mass loss and N reflects the long-time corrosion behavior. The values of the parameters A and N were obtained by a least-squares regression for all the samples investigated. We determined that for the samples investigated here, $N > 1$ always and V increases with time throughout the experimental duration. In this paper we summarize the experimental results and discuss the effect of A and N on corrosion rate and the relationship between the corrosion current density and the parameters A and N.

I. INTRODUCTION

The influence of ion beam treatment on the corrosion behavior of metals and alloys has been studied by a number of workers [1-6]. Previous work by us has focused on systematic studies of the electrochemical corrosion behavior of Fe-based alloys treated by ion beams [4-8]. The kinetic investigation of corrosion is usually carried out using the polarization electrochemical method. The corrosion current density i_{cor}, which is directly related to the corrosion rate, can be obtained from simplification of the following general equation [9]:

$$I = i_{cor}[\exp(\beta nF\Delta E/RT) - \exp(-\alpha nF\Delta E/RT)] \tag{1}$$

where I is the circuit current density, α and β are constants (with the restriction $\alpha + \beta = 1$), n is the valence, F is the Faraday constant, ΔE is the polarized potential, R is the gas constant and T is the absolute temperature.

When the structure and composition of the metal are homogeneous, i_{cor} can usually be regarded as a constant independent of the holding time in the solution and the polarized potential ΔE. But for a metal or alloy subjected to surface ion beam treatment, the implanted element in the treated surface layer is distributed approximately Gaussian according to the LSS theory [10], and the irradiation damage also has a depth distribution. That is, the structure, composition and defect density in the treated layer are not uniformly distributed with depth. These factors give rise to a variation in i_{cor}. Although implantation using the Mevva implantation facility [11] results in a somewhat more uniformly distributed layer, the structure and composition in the treated layer, transition layer and base material are still different. Thus there is a limitation in the investigation of corrosion kinetics of surface treated metals or alloys using the polarized electrochemical method, and one cannot obtain the corrosion current density at any arbitrary time or position in the layer. In principle a mass loss method could be better, but in practice such a method might be limited by its

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precision. In view of these considerations, we have investigated the corrosion kinetics by the mass loss method, using high precision atomic absorption spectroscopy for determination of mass loss. The present paper is part one of a series studying the corrosion resistance to acid solution of Fe-based alloys that have been ion beam modified; the emphasis is on the corrosion kinetics so as to reveal surface modification mechanisms.

II.   EXPERIMENTAL

Sample preparation

The samples studied were pure iron, 18-8 Cr-Ni stainless steel, and medium carbon steel (0.45% C). The materials were forged into rods 10 mm in diameter, annealed for 30 minutes at 920°C and slowly cooled to obtain uniform microstructure. Samples of 5 mm thickness were cut from the rods and carefully polished and cleaned. A number of samples were film-deposited in a vacuum depositor (5×10^{-5} Torr), and the film thickness determined by a micro-balance with a precision of 10^{-6} gm.

Ion beam bombardment

Specimens were cleaned in alcohol immediately prior to implantation. Ion implantation was carried out using a Mevva facility [11]. The mean ion energy was near 100 keV and the dose was up to 1×10^{17} cm^{-2}. The target temperature was maintained below 200°C. Implanted species included the corrosion resistant elements Ti, Cr, Cu, Ni, Mo, Yb and B; the boron was implanted using another implanter.

Measurements

All specimens, both implanted and reference unimplanted, were sealed in wax so as to leave only the polished or treated surface exposed and then soaked in an acid solution (1N H_2SO_4

for the medium carbon steel and 20% for 18-8 and pure iron). The mass of the dissolved elements was measured accurately as a function of time by means of atomic absorption spectroscopy. The soaking time in our experiments was up to 48 hours. All our experiments have indicated that the corrosion is uniform.

III. RESULTS

Kinetic curves showing the corrosion data — mass loss Q *vs* soaking time t — for some of the samples are shown in Figure 1. For our experimental conditions, all of the treated and untreated samples show the same general shape of kinetic curve.

Measurements for all samples reveal the interesting fact that the data curves have up-concavity instead of down-concavity as might be expected, meaning that the slope of the curve increases with increasing soaking time. In addition, from the original curves we know that $dQ/dt \rightarrow 0$ as t and $Q \rightarrow 0$. Therefore a functional relationship of the form

$$Q = At^N \tag{2}$$

suggests itself, where A and N are constants independent of soaking time. Because of the up-concavity of the data curves ($d^2Q/dt^2 > 0$), we also know that N must be greater than unity. We can verify the appropriateness of Eq. (2) by fitting the data to Eq. (2) in logarithmic form:

$$\log Q = \log A + N \log t; \tag{3}$$

a plot $\log Q$ *vs* $\log t$ should thus be a straight line. We have analyzed the data in this way and have found that there is a good linear relationship between the logarithms of mass loss and soaking time,

confirming the description given by Eq. (2). Log plots corresponding to the data of Figure 1 are shown in Figure 2.

A linear regression using Eq. (3) shows that the data fit the description of Eq. (2) with a mean error of less than 3% and that N > 1 (up to 3) for all samples. For some samples there are two N values (see Figure 2). Different N values should correspond to different surface layer structures; this will be discussed further elsewhere.

From Eq. (2) we have an expression for the corrosion rate V,

$$V = dQ/dt = ANt^{N-1}. \tag{4}$$

Because N > 1, the corrosion rate is not constant. Figure 3 shows the corrosion rate as a function of soaking time according to Eq. (4), based on the regressed values of A and N.

Evaluation of the corrosion rate for all the samples indicates that high dose, multi-element implantation of Cr + Mo + Cu can improve the corrosion resistance to acid solution of medium carbon steel and 18-8 steel, and boron implantation increases the corrosion resistance of pure iron in the near-surface layer but decreases it for long soaking times. We found that the surface 18-8 alloy produced by multi-element implantation has a much higher corrosion resistance than conventional 18-8 steel, and also that implantation of Cr + Mo improves the corrosion resistance of pure iron significantly.

The thickness of the surface modified layer is of order 1000 Å according to classical implantation theory [10], but the corrosion measurements imply that there are implanted elements far deeper than this. One interpretation of this observation is that the implanted elements have a lower dissolving rate than Fe atoms and appear to migrate inward during corrosion, thus having a

sustained effect on the corrosion behavior of the base material. We plan to study this effect in the future.

IV.   DISCUSSION

The parameters A and N

The influence of ion implantation on the corrosion behavior is displayed by its effect on the parameters A and N, and is expected to be related to changes in surface structure, composition and defects; we will investigate this connection in future work. Here we consider the effect of the values of A and N on the corrosion behavior.

According to Eq. (4), the greater the values of A and N, the greater the corrosion rate. A and N have different effects on the corrosion. The parameter A is numerically equal to the mass loss in the initial unit soaking time, or the corrosion rate when $N = 1$. Thus the parameter A is a measurement of the initial corrosion resistance; a high A value means low corrosion resistance. The value of A dominates the corrosion behavior for short soaking times.

For early times, high values of the parameter N indicate high corrosion resistance (low corrosion rate), as shown in Figure 4. The value of N determines the time rate of change of the corrosion rate, and has a greater effect on the corrosion-resistant lifetime than does the parameter A. For long soaking times, the corrosion behavior is mainly determined by N; high N values indicate low corrosion resistance. Thus the value of N determines the long-time corrosion behavior and the corrosion time variation.

Summarizing, low A values and high N values during the initial stages, and low N values in later stages, indicate high corrosion resistance of materials.

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Corrosion current

When a sample is soaked in acid solution it dissolves according to the oxidation reaction

$$M \rightarrow M^{+n} + ne \tag{5}$$

where M represents a metal element, n the valence of the metal, and e the electronic charge. At the same time the hydrogen (H^+) in solution is reduced. Both reactions should be equal. According to classical electrochemical theory [9], we have

$$i_{cor} = nFKC_M \exp(-W/RT) \tag{6}$$

where K is a reaction constant, C_M the concentration of reacting metal element and W the reaction activation energy. In the surface layer, the transition layer and the base material of the treated specimen, the composition, structure and defect density are not homogeneous, as mentioned above. Even for the unimplanted samples, there inevitably exists a native oxide film on the surface. Thus i_{cor} is not expected to be constant.

It is clear that

$$Q = \int_0^t (m / nF) i_{cor} dt \tag{7}$$

and

$$V = dQ/dt = (m/nF)i_{cor} \tag{8}$$

where m is the molar atomic weight. Combining Eqs. (4) and (8) we obtain

$$i_{cor} = (nF/m)ANt^{N-1}. \tag{9}$$

This indicates how the corrosion current density is related to the soaking time. For unit exposed surface area,

$$Q = \rho x \tag{10}$$

where ρ is the metal density and x the uniform corrosion depth. Now combining Eqs. (2), (9) and (10), we have

$$i_{cor} = (nF/m)NA^{1/N}(\rho x)^{(N-1)/N} \tag{11}$$

Eq. (11) reveals the relationship between i_{cor} and the depth below the surface. The corrosion current value obtained by the polarization electrochemical method according to Eq. (1) is in fact an average value for the layer corresponding to one sweep. This value should be equal to the mean value of i_{cor} given by

$$\bar{i}_{cor} = (nF/mX)NA^{1/N}\int_0^X (\rho x)^{(N-1)/N}dx$$
$$= [nFN^2/m(2N-1)]A^{1/N}(\rho X)^{(N-1)/N} \tag{12}$$

where X is the thickness corresponding to one sweep in the electrochemical measurement. We have compared the values of i_{cor} obtained in these two ways and good agreement is obtained. This study will be described elsewhere.

Finally, by combining Eqs. (6) and (12) we see that the parameters A and N are not directly related to the valence n, but strongly related to the activation energy and reciprocal absolute temperature T as follows,

$$N^2 A^{1/N} = (2N-1)mK\overline{C}_M (\rho X)^{N/(N-1)} \exp(-W / RT) \qquad (13)$$

where $\overline{C}_M$ is the mean concentration of the reacting metal element within a layer of thickness X. By obtaining the values of A and N at different temperatures, we can determine the reaction activation energy W from Eq. (13). We will explore this possibility in future work.

V. CONCLUSIONS

1. The mass loss is well described as a function of soaking time by a power law variation, for all samples and under our experimental conditions. The value of the power index parameter for all samples lies between 1 and 3.

2. The corrosion rate increases with increasing soaking time.

3. Multi-element implantation significantly improves the resistance to corrosion by acid solution of pure iron, 18-8 steel and medium carbon steel.

4. The parameters A and N are not directly related to the valence but strongly related to the activation energy and absolute temperature.

REFERENCES

1. C. J. McHargue, International Metals Reviews, 31(2), 1986.

2. F. A. Smidt, Nucl. Instrum. Methods B, (1985) 532.

3. F. A. Smidt, Ion Implantation and Materials Processing, (Noyes, Park Ridge, NJ, 1983), p. 181.

4. Tian Wei, Li Jiun, Cao Niansen and Cai Weiping, Nucl. Instrum. Methods B21 (1987) 597.

5. Tian Wei, Cai Weiping, Li Jiun and Wu Run, Mater. Sci. & Eng. A116 (1989) 21.

6. Tian Wei, Cai Weiping, Li Jiun and Wu Run, Mater. Sci. & Eng. A116 (1989) 15.

7. Tian Wei, Cai Weiping, Beam-Solid Interactions:Physical Phenomena, Mat. Res. Soc. Symp. Proc. 157 (1990) 239.

8. Tian Wei, Cai Weiping, Thin Films and Beam-Solid Interactions, C-MRS Symp. Proc. ᒥ (1990) 523.

9. M. C. Fontana and N. D. Greene, Corrosion Engineering, (McGraw Hill, 1978).

10. P. D. Townsend, J. C. Kelly and N. E. W. Hartley, Ion Implantation, Sputtering and their Applications, (Academic Press, London, 1976).

11. I. G. Brown; see, for instance, paper presented at this conference, "Versatile High Current Metal Ion Implantation Facility".
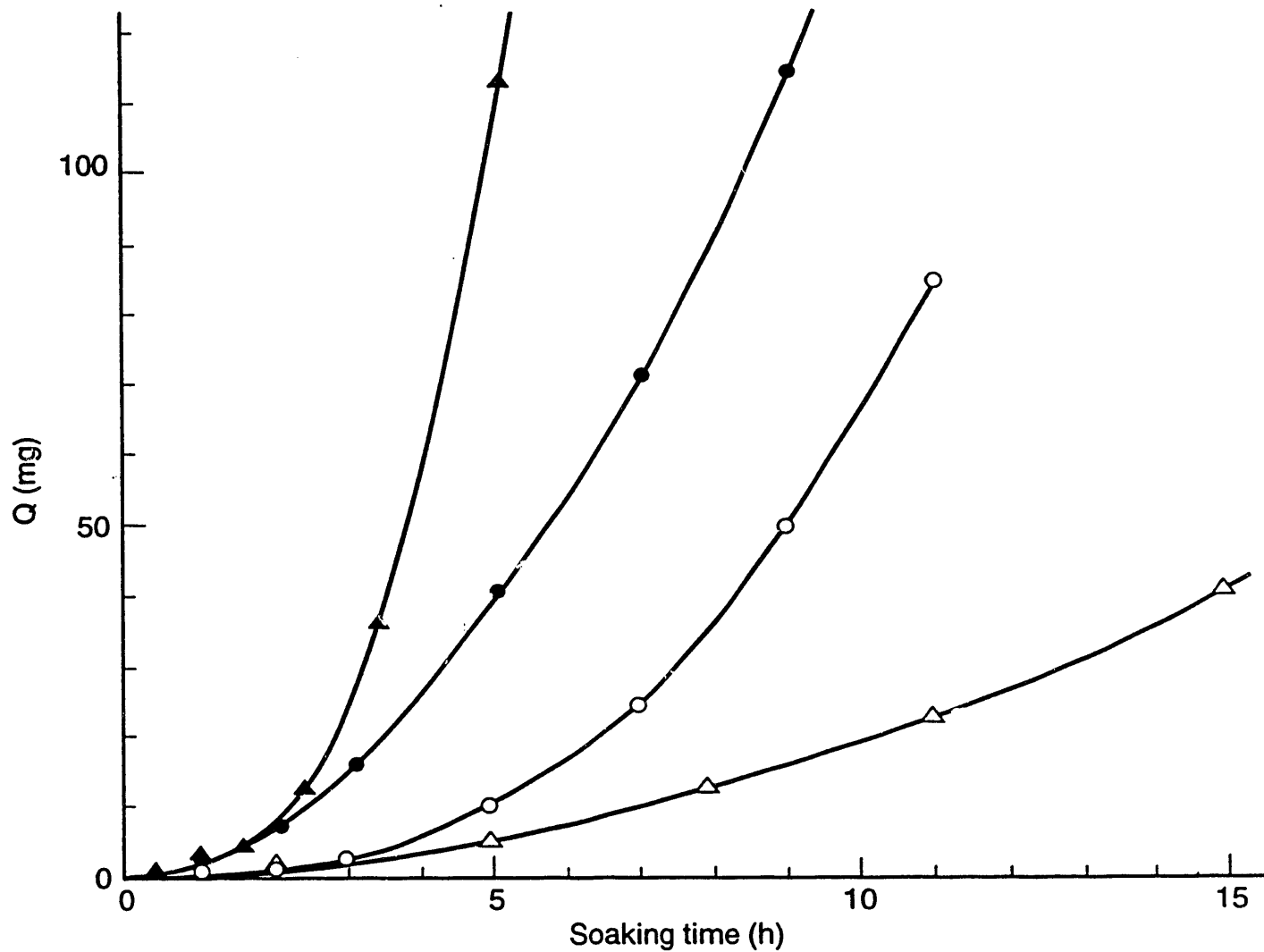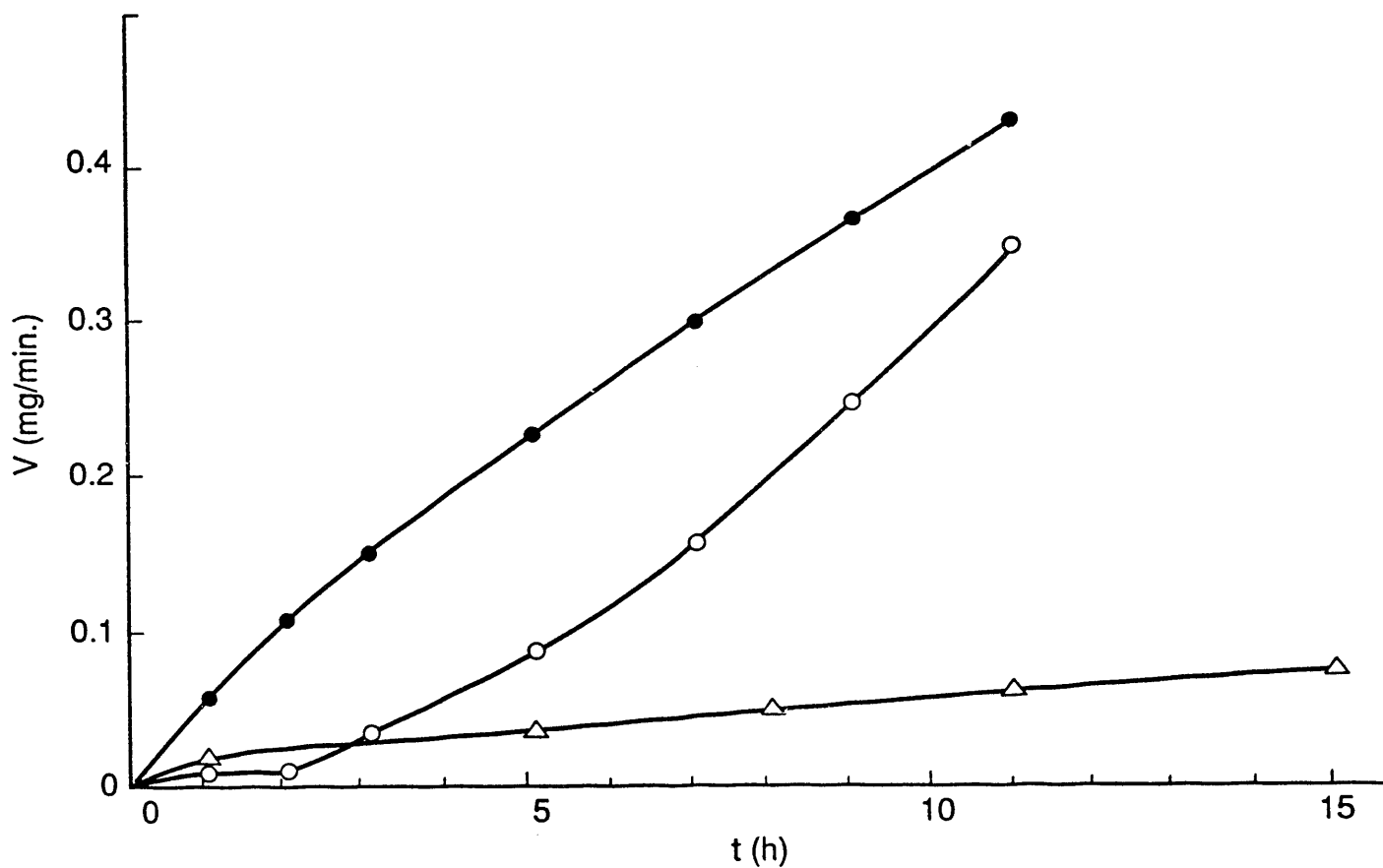
XBL915-6972

Fig. 1   Mass loss Q as a function of soaking time t. Typical curves for some of the samples
investigated. (XBL 915-6972)

|	
Full circles:	unimplanted 18-8 stainless steel;
Open circles:	18-8 stainless steel implanted with
	Cr (1×10^{17}) + Cu (7×10^{16}) + and Mo (7×10^{16});
Full triangles:	medium carbon steel implanted with
	Cr (1×10^{17}) + Cu (7×10^{16}) + and Mo (7×10^{16});
Open triangles:	Fe/Cr implanted with B (1×10^{17});
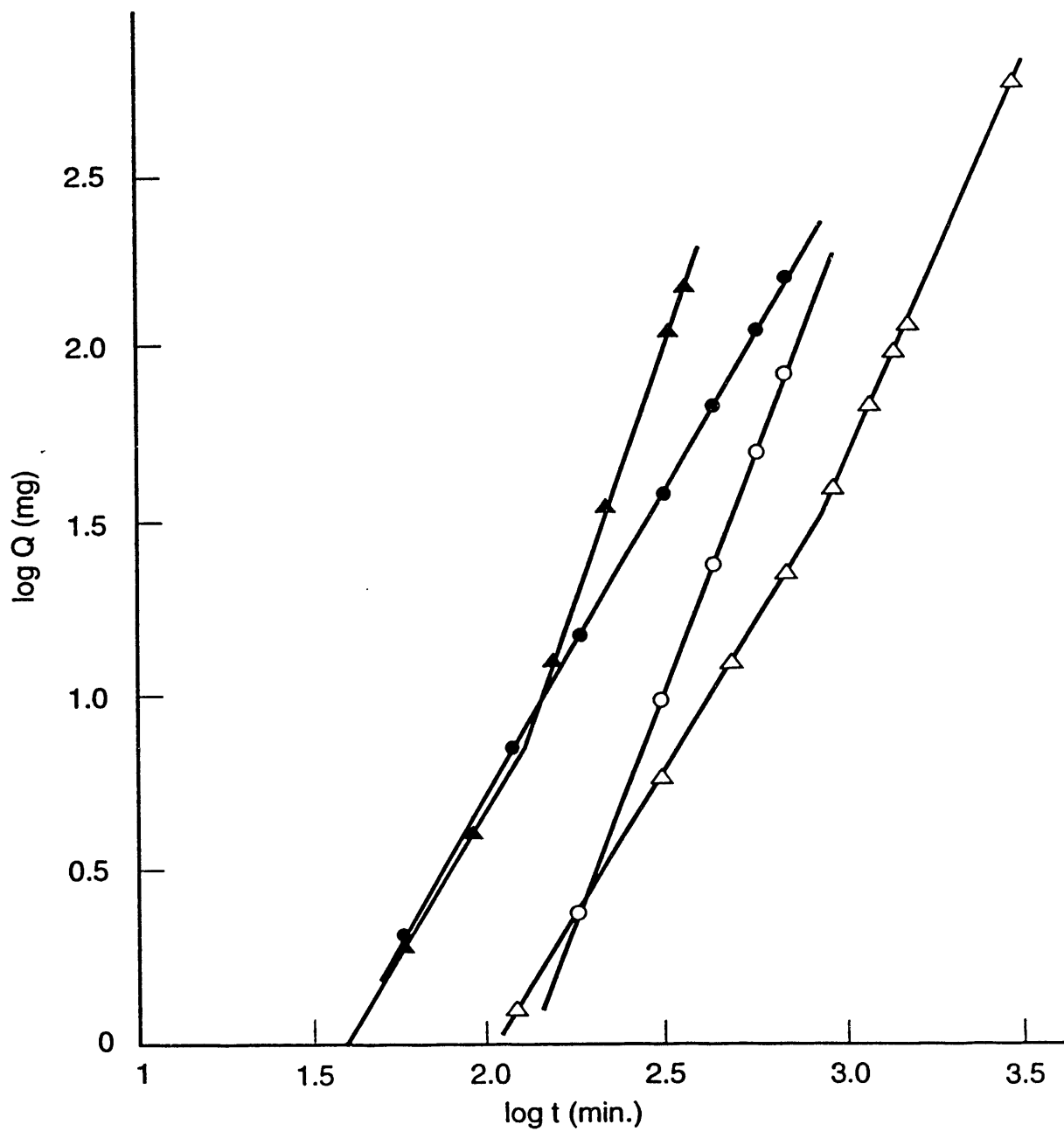
Fig. 2 Data of Figure 1 plotted logarithmically: log Q *vs.* log t. (Same symbols as for Fig. 1.)
(XBL 915-6973)

13

XBL915-6974

Fig. 3 Corrosion rate V as a function of soaking time t for the same samples as given in Figs 1
and 2. (Same symbols as for Fig. 1.) (XBL 915-6974)

Q

A

N=1

N1
N2
N3
N4

t

1
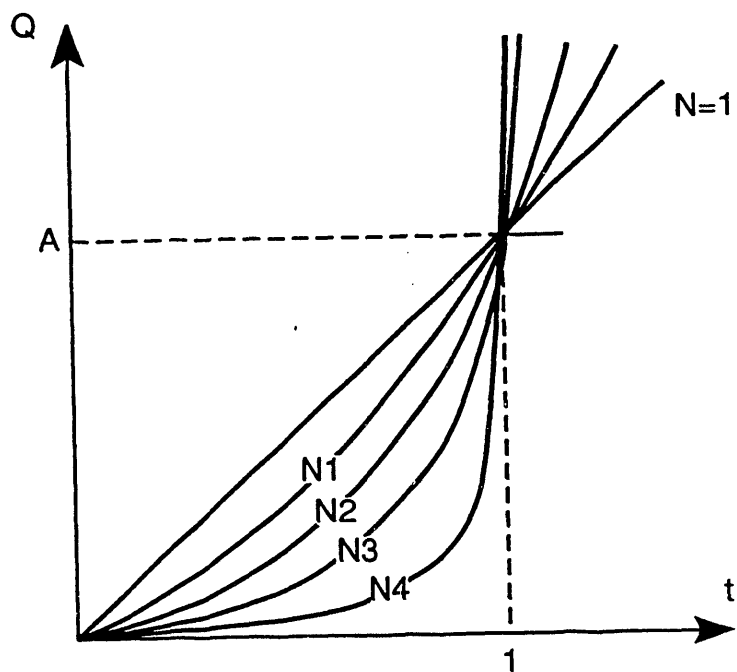
XBL 915-6975

Fig. 4   Schematic diagram of the effect of different N values on the mass loss Q as function of time t, for constant A. ($N_4 > N_3 > N_2 > N_1 > N$). (XBL 915-6975)

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