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Influence of Multi-Element Ion Beam Bombardment on the Corrosion Behavior of Iron and Steel

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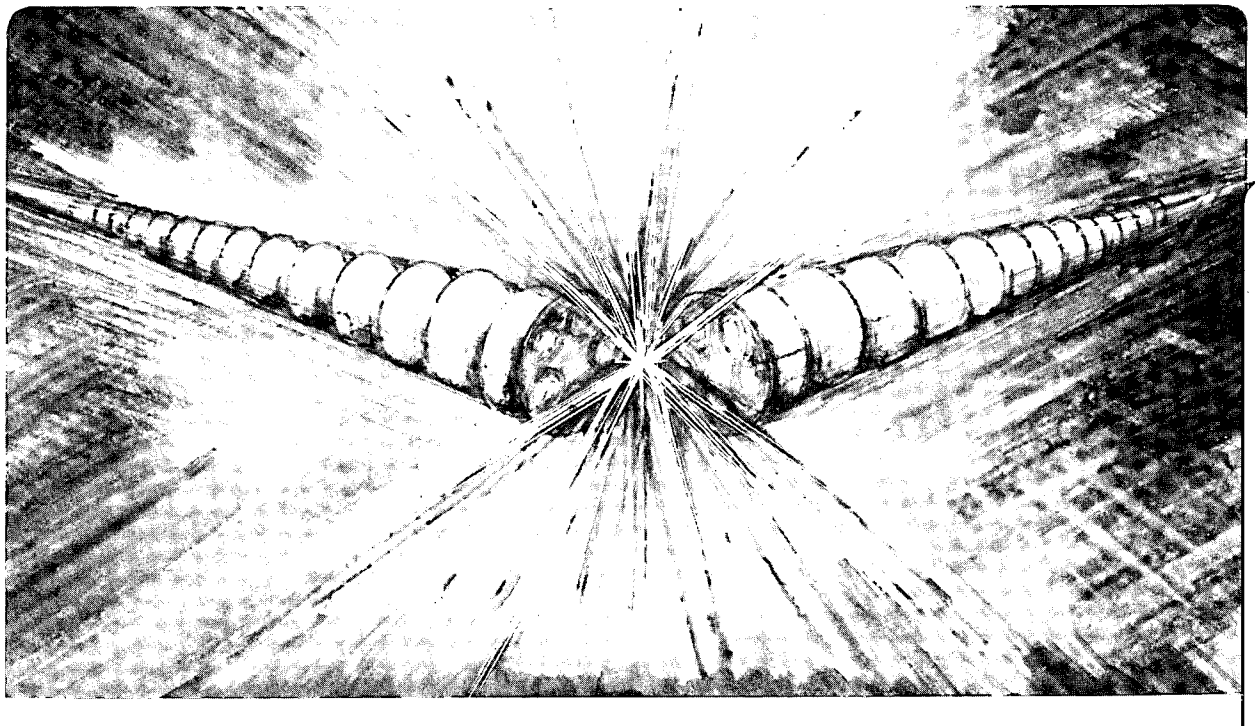

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INFLUENCE OF MULTI-ELEMENT ION BEAM BOMBARDMENT ON THE CORROSION BEHAVIOR OF IRON AND STEEL

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ABSTRACT

The effect of multi-element ion implantation on the corrosion resistance to acid solution has been studied for stainless steel, medium carbon steel, pure iron, and chromium-deposited iron. The implanted elements were Cu, Mo, Cr, Ni, Yb and Ti at doses of each species of from 5×10^{15} to 1×10^{17} cm^{-2} and at ion energies of up to 100 keV. The stainless steel used was 18-8 Cr-Ni, and the medium carbon steel was 0.45% C. The implanted samples were soaked in dilute sulfuric acid solution for periods up to 48 hours and the weight loss measured by atomic absorption spectroscopy. The kinetic parameter values describing the weight loss as a function of time were determined for all samples. In this paper we summarize the corrosion resistance behavior for the various different combinations of implanted species, doses, and substrates. The influence of the composition and structure of the modified surface layer is discussed.

I. INTRODUCTION

We have previously investigated the effect of single-element ion bombardment on the corrosion behavior of iron and steel, and the results of this work have been reported elsewhere [1-4]. Other workers have reported that multi-element ion bombardment produces different effects from single-element bombardment on the properties and characteristics of the modified surface [5,6]. Here we report on our studies of the effect of multielement ion implantation using a Mevva facility [7] on the corrosion resistance to acid solution of stainless steel, medium carbon steel and iron.

II. EXPERIMENTAL

Sample preparation

The materials chosen to study were 18-8 Cr-Ni stainless steel, medium carbon steel with carbon content 0.45%, and pure iron. All samples were prepared by forging the initial rod, cutting, metallographically abrading, polishing to a mirror finish, cleaning and drying.

Ion implantation

The implanted species were Cu, Mo, Cr, Ni, Yb and Ti, and were chosen for their beneficial effects on corrosion resistance. The implantation doses were determined by reference to the composition of corrosion resistant alloys, which fall in the range from 5×10^{15} to 1×10^{17} cm^{-2}. The implantations were done using a Mevva facility [7] at ion energies up to approximately 100 keV. Table I shows the implantation conditions.

Mass loss measurements

All samples, both implanted and unimplanted, were soaked in acid solution for periods up to 48 hours and the mass loss was measured by atomic absorption spectroscopy as a function of soaking time. Because of their low resistance to corrosion by acid, the medium carbon steel samples were soaked in a 1N H_2SO_4 solution and the Fe and 18-8 Cr-Ni samples in 20% H_2SO_4 solution. The temperature of the solution was thermostatically controlled to 40°C

III. RESULTS

The results of measurements for all samples are shown in Figures 1 - 3. All of the implanted samples have a higher corrosion resistance than the corresponding unimplanted samples, except for the sample F8 (Cr + Mo implantation) which shows much lower corrosion resistance than F1.

The mass loss measurements Q are well fitted by the expression

$$Q = At^N \tag{1}$$

where A and N are parameters [8]. Figure 4 shows the fit of the data to Eq. (1), plotted logarithmically as log Q *vs* log t. Thus we obtain the values of the parameters A and N for all samples by obtaining the best fit of the data to Eq. (1) [8], and the results are shown in Table II. From the values given in Table II we can also obtain the variation of corrosion rate V with soaking time, obtained from the following expression derived from Eq. (1),

$$V = ANt^{N-1} \tag{2}$$

Some typical curves of V *vs* t are seen in Figure 5.

IV. DISCUSSION

In order to produce a more uniform acidfast surface alloy, we chose to implant at two different implantation doses. Iron and steel are low potential materials, and when they are soaked in acid solution, H^+ depolarization occurs; i.e., the cathodic reaction produces H_2. They are also passive materials and their passive films, known to be Fe_2O_3 in H_2SO_4 solution, are alkaline. In a certain potential region the oxide films exhibit passivation in the acid solution. But the oxide of Mo is significantly acidic, and when it is soaked in acid solution, it is passivated rapidly [6]. Mo^+ implantation can improve acidity-resistance of iron and steel in acid solution. Thus it is beneficial for corrosion resistance.

The improvement of medium carbon steel to corrosion resistance is not only because the implanted Cr, Cu and Mo are strongly corrosion-resistant, but also because the implantation doses are sufficiently high to form an amorphous layer, which obviously increases the corrosion resistance [1-3]. For the same reason, implantation with high doses of Cu + Mo increases the corrosion resistance of 18-8 steel in acid solution, and additional Cr implantation to a higher dose improves the corrosion behavior further (see Figure 3).

When the Cr content is lower than 12%, the structure of the passive film is an incomplete spinel type (6). This decreases the acidfast characteristics. If the Cr content of the surface is sufficiently high (>19%), then the surface structure changes from spinel to glassy and the corrosion resistance increases significantly.

The sample F8, implanted with Cr (5×10^{16}) + Mo (5×10^{15}), was found to exhibit much lower corrosion resistance than the sample F1 without implantation (see Figure 1). The implantation dose and energy were such that the surface concentrations of Cr and Mo were about 13 at% and 1.3 at%, respectively. We would thus have expected the corrosion resistance to be improved rather than decreased. As a provisional explanation of this anomalous result we hypothesize that the implantation dose was not high enough to form an amorphous layer, and that multiple phases induced by the ion implantation cause the corrosion resistance to decrease. Additionally, the defect density induced may be still high enough to decrease the corrosion resistance.

Finally, the surface composition of the sample F9 was determined from the implantation dose to be about the same as that of 18-8 steel. But the former is much more corrosion-resistant than the latter; compare the results for sample F9 in Figure 1 with the sample 181 data of Figure 3. We ascribe this to the formation of a smooth, amorphous surface layer in the implanted specimen due to high dose ion bombardment.

V. CONCLUSION

1. High dose ion implantation of Cr + Mo + Cu significantly improves the corrosion resistance of medium carbon steel in 1N H_2SO_4 solution (at 40°C).

2. The corrosion behavior of 18-8 Cr-Ni steel in 20% H_2SO_4 solution (at 40°C) is improved by implantation of Cu + Mo, and is further improved by additional Cr implantation.

3. Cr + Mo ion implantation decreases the corrosion resistance of pure iron in 20% H_2SO_4 solution (at 40°C) under our implantation conditions.

4. "Synthetic" stainless steel formed as a surface layer on pure iron by multi-ion implantation is of much higher corrosion resistance than is the corresponding bulk stainless steel; we ascribe this to the formation of an amorphous surface layer due to ion bombardment.

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Table I. Implantation conditions

Sample	Substrate	Ion Implantation Conditions
F1	Fe	No implantation
181	18-8 st. steel	No implantation
451	.45% C steel	No implantation
F8	Fe	Cr (5×10^{16}, 50 keV) + Mo (5×10^{15}, 55 keV)
F9	Fe	Yb (1×10^{15}, 80 keV) + Ni (3×10^{16}, 55keV) + Cr (5×10^{16}, 40 keV) + Ti (5×10^{15}, 38 keV)
182	18-8 st. steel	Cu (3×10^{16}, 34 keV) + Cu (5×10^{16}, 68 keV) + Mo (3×10^{16}, 47 keV) + Mo (5×10^{16}, 95 keV)
183	18-8 st. steel	Cr (1×10^{17}, 36 keV) + Cr (5×10^{16}, 73 keV) + Cu (5×10^{16}, 34 keV) + Cu (2×10^{16}, 68 keV) + Mo (5×10^{16}, 47 keV) + Mo (2×10^{16}, 90 keV)
452	.45% C steel	Cr (1×10^{17}, 36 keV) + Cr (5×10^{16}, 73 keV) + Mo (5×10^{16}, 47 keV) + Mo (2×10^{16}, 90 keV) + Cu (5×10^{16}, 34 keV) + Cu (2×10^{16}, 68 keV)

Table II. Values of parameters A and N for all samples

Sample	$A_1 \times 10^3$ (mg)	N_1	t_0 (min)*	$A_2 \times 10^3$ (mg)	N_2
F1	10.48	1.32	900	0.40	1.80
F8	132.20	1.30	270	3.78	1.91
F9	30.50	1.0	600	0.014	2.18
451	4.60	1.95			
452	0.94	1.88	120	5.90	2.92
181	1.34	1.80			
182	16.0	1.20	150	0.40	1.94
183	2.10	1.30	150	0.0015	2.75

* when $t \lesssim t_0$, $Q = A_1 t^{N_1}$; and when $t > t_0$, $Q = A_2 t^{N_2}$

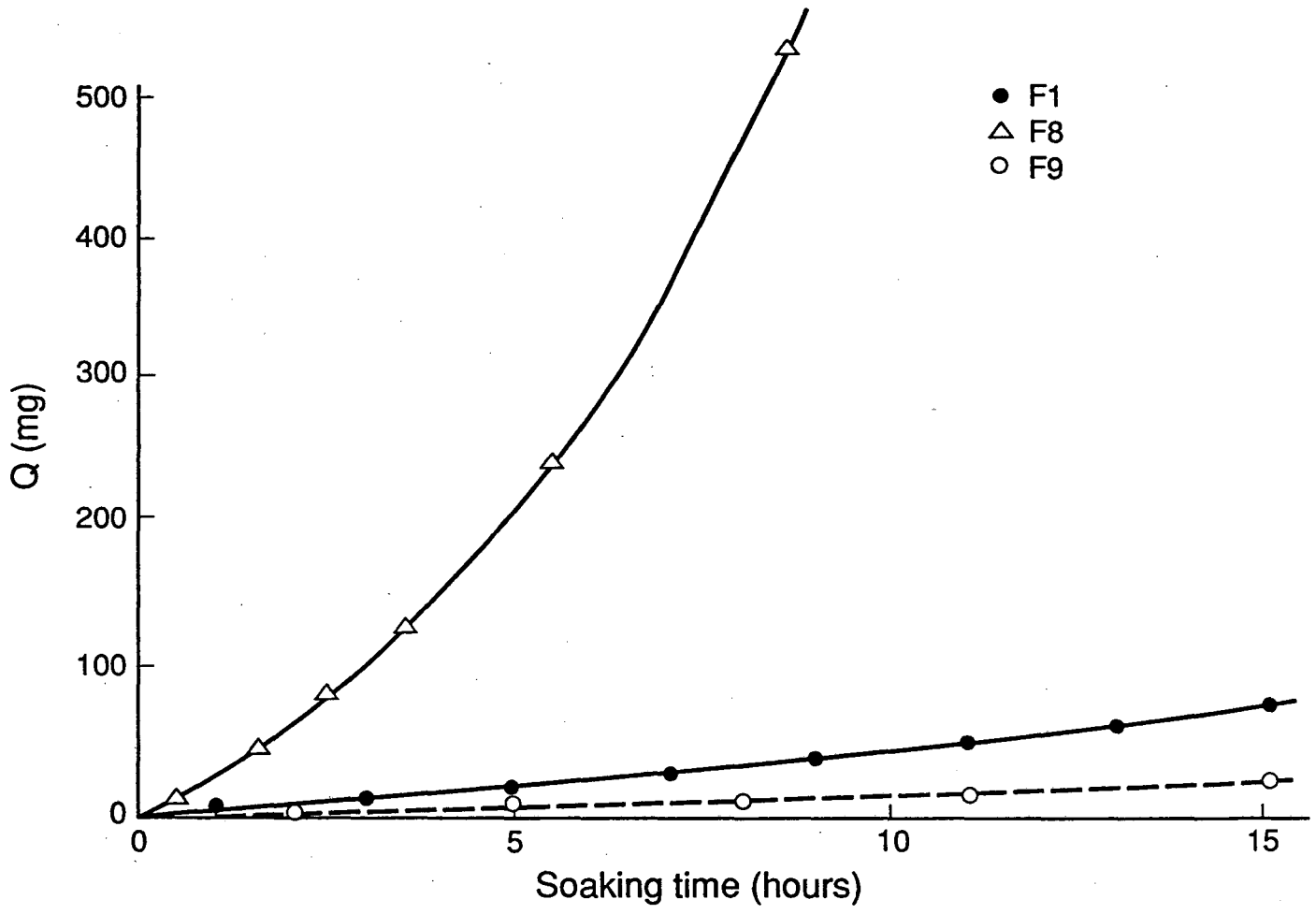

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Fig. 1 Mass loss Q as a function of soaking time t for samples F1, F8 and F9.

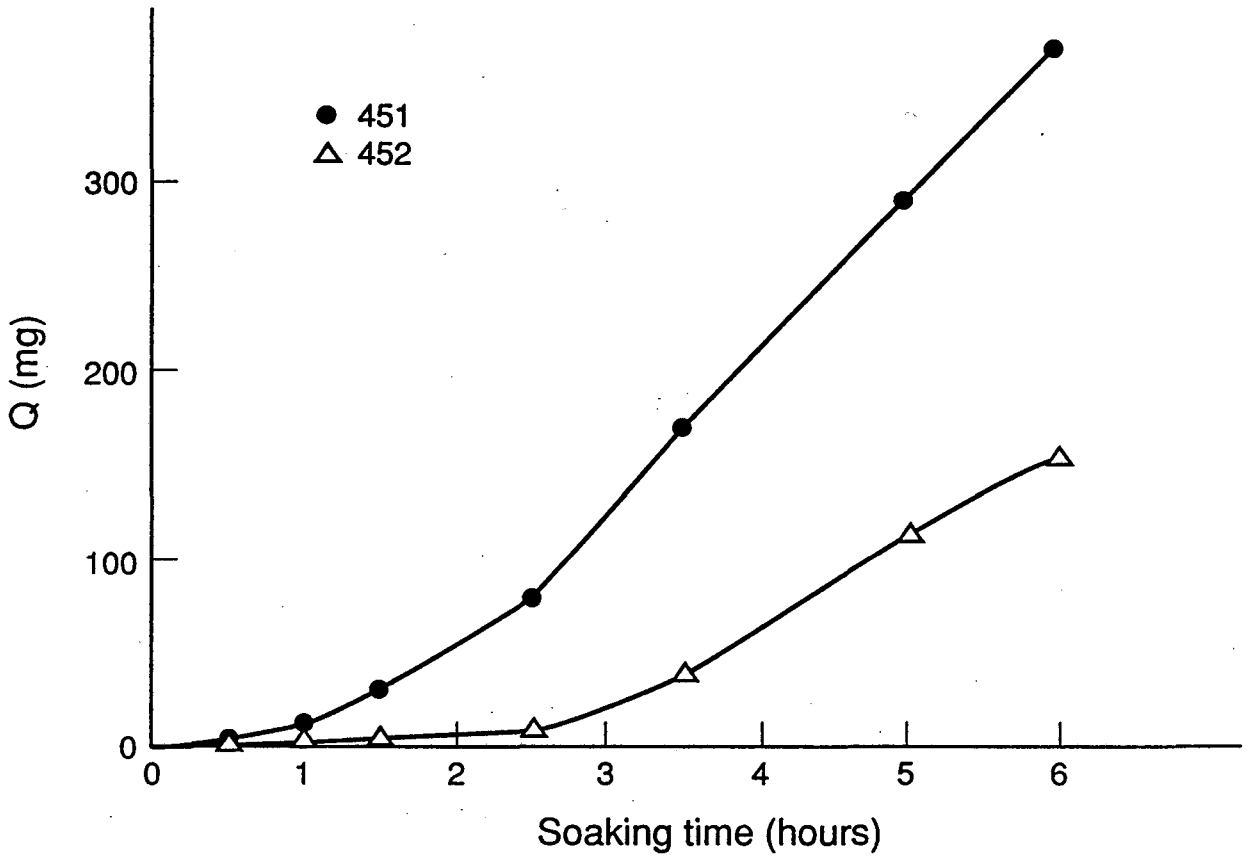

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Fig. 2 Mass loss Q as a function of soaking time t for samples 451 and 452.

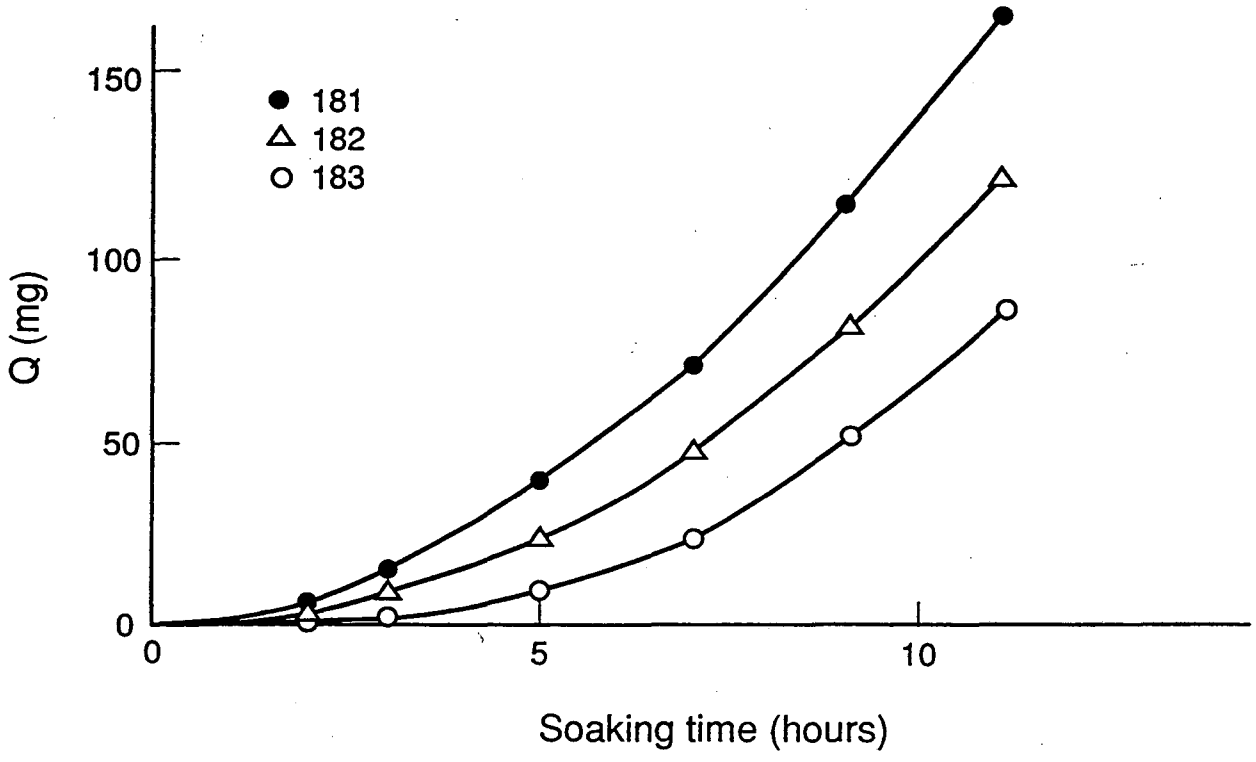

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Fig. 3 Mass loss Q as a function of soaking time t for samples 181, 182 and 183.

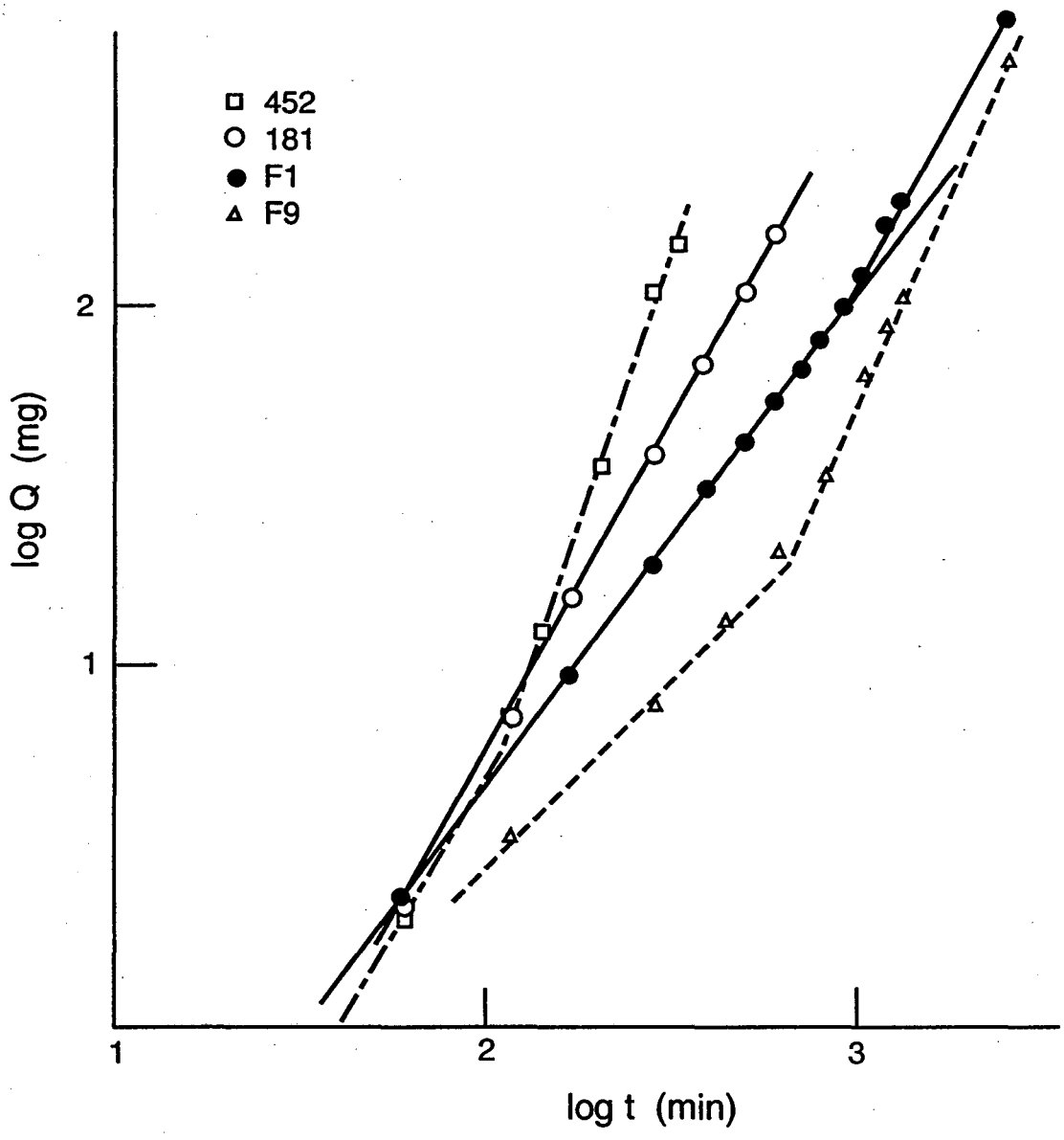

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Fig. 4 Log Q *vs.* log t for samples F1, F9, 181 and 452.

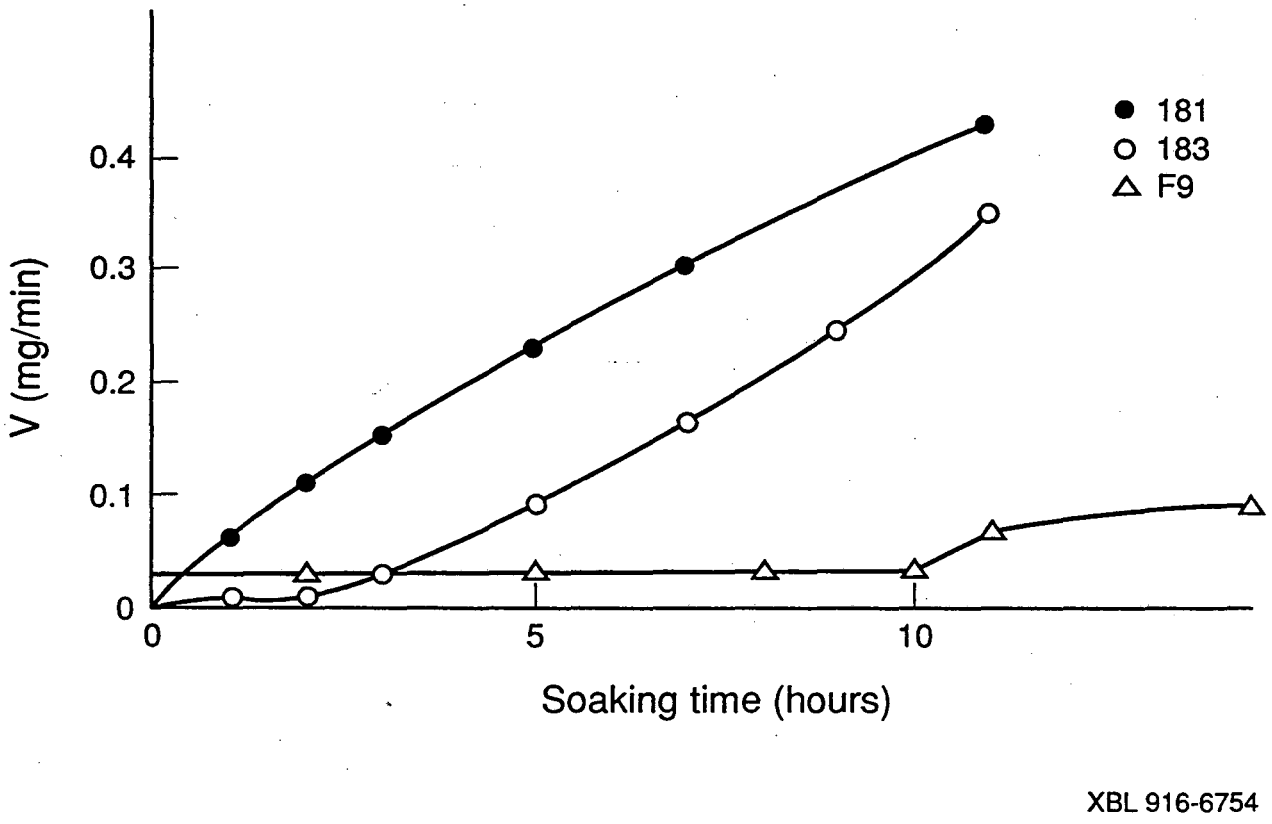

Fig. 5 Corrosion rate V as a function of soaking time t for samples F9, 181 and 183.

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