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An Electrochemical Method for Determining Hydrogen Concentrations in Metals and Some Applications

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and Space Administration

**Scientific and Technical
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TECHNICAL PAPER

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INTRODUCTION

The importance of hydrogen induced failure of materials has been widely recognized. Catastrophic failure of high strength steel parts, such as aircraft landing gears, can often be attributed to hydrogen embrittlement. The source of hydrogen which causes failure in the presence of stress can be a corrosion reaction but can also be a pretreatment process such as a pickling, a welding, or a plating process.

Since the important role of hydrogen in the catastrophic failure of metal has been recognized, a great interest exists in developing methods for the determination of hydrogen concentrations, which are fairly low in many cases, in metallic structures. A device, termed the "barnacle electrode," for determining the hydrogen concentration in steels has been developed and evaluated by DeLuccia, Berman, et al. [1,2], which is based on the electrochemical permeation technique [3,4]. The device, which was described by Mansfield, et al. [5], has met with a great deal of success. It was the purpose of the present work to develop a similar electrochemical technique for the measurement of hydrogen using the EG&G-PARC Model 350A Corrosion Measurement System and to present a series of results concerning hydrogen uptake, elimination by baking, uptake during electroplating, and the effect of heat treatment for high strength steels.

BACKGROUND OF MEASUREMENT

The basis for measurement of hydrogen concentration, C_0, is an electrochemical permeation method which was first described by Devanathan and Stachurski [3,4], for determination of C_0 and the diffusion coefficient D of hydrogen. In this method, hydrogen is produced on one side of a metal foil, either as the result of a corrosion reaction in acidic media, or by application of a cathodic current. On the other side of the foil, hydrogen which has diffused through the metal is removed by application of an anodic constant potential which leads to oxidation of the hydrogen to water. The measurement is carried out in an alkaline solution. Under the assumption that semi-infinite diffusion occurs in a sample of finite thickness, the solution of the diffusion equations:

$$I = -ZFD \left(\frac{\partial C}{\partial X} \right)_{x=0} \quad , \tag{1}$$

$$\frac{\partial^2 C}{\partial X^2} - \frac{1}{D} \left(\frac{\partial C}{\partial t} \right) = 0 \tag{2}$$

leads to the well known Cottrell equation for the permeation current I_p:

$$I_p = ZFC_o \left(\frac{D}{\pi t}\right)^{1/2} \tag{3}$$

Here, Z is the number of electrons involved in the reaction (one), F is the Faraday constant, D is the diffusivity of hydrogen through the metal, and I_p is the current density at time t. Equation (3) holds for a maximum measurement period t max = $L^2/4D$. For AISI 4340 steel, for which D = 2.5×10^{-7} cm^2/sec, t max = 10^4 sec for a sample thickness L = 1 mm.

The hydrogen concentration can be determined from a plot of log I_p versus log t in the form:

$$\log I_p = \log \frac{ZFD^{1/2}}{\pi^{1/2}} C_o - 1/2 \log t \quad . \tag{4}$$

The plot is a straight line with slope −1/2. Such a plot is shown in Figure 1 for AISI 4130 steel.

For AISI 4340 steel, for which D = 2.5×10^{-7} cm^2/sec, equation (4) reduces to:

$$\log C_o = \log I_p + 1/2 \log t - 2.33455 \quad . \tag{5}$$

Here, t is the time in seconds, I_p is the diffusion current density in μA/cm^2, and C_o is the hydrogen concentration in parts per million (ppm). The measured current contains additional contributions from the passivation process (and any other oxidation process). However, these contributions decay with t^{-1}, while I_p decreases with $t^{-1/2}$. At longer time periods, the measured current therefore contains less contribution from the passivation process, and it is advantageous to measure current after a longer time period, e.g., 30 min, in order to reduce this contribution.

EXPERIMENTAL

The EG&G-PARC Model 350A corrosion measurement console was employed for all measurements in this work, with emphasis being placed on the development of a successful technique for measuring hydrogen concentrations. Results are presented which examined the feasibility of applying measurements of hydrogen concentrations in hydrogen uptake studies to manufacturing processes such as electrolysis and electroplating, hydrogen elimination, and heat treatment.

The sample holder employed in this study is shown in Figure 2 and the cell assembly in Figure 3. Preliminary to any experimental measurements, samples, which were 5/8 in. in diameter and approximately 1/16 in. thick, were wet sanded with 400 grit silicon carbide paper and degreased in boiling trichloroethylene. Samples were not subjected to further surface preparation techniques after the initial hydrogen uptake or elimination treatment in order to preserve concentration effects. During the potentiostatic measurements, the cell, containing a 0.2 N NaOH solution, was controlled thermostatically at 30°C in a constant temperature bath. Although a constant potential of -0.600 V (SCE) has been recommended by previous investigators for these measurements, a potential of 0.0 V (SCE) was utilized to reduce the passivation current. Samples were placed in the sample holder and allowed to stand in solution for 1 hr before initiating the potentiostatic run. This was necessary to allow the observed corrosion potential to reach its equilibrium value so that reproducible values of the sample blank could be obtained. After initiation of the potentiostatic run, a period of 30 min was allowed for current decay before a reading was taken, at which time the observed current was recorded. Before hydrogen uptake from any source, blanks were first run on samples to obtain the contribution of current from the passivation process. This value was subtracted from the value for the hydrogen containing sample after it was subjected to hydrogen uptake and a subsequent potentiostatic measurement made. As a result, the measured current, after subtraction of the blank value, should be the contribution due to hydrogen only. The successful test of equation (4) using type AISI 4130 steel using these procedures is shown in Figure 1.

For hydrogen uptake studies, heat treated AISI 4340 steel was electrolyzed for various lengths of time in 0.1 N H_2SO_4 at a current density of 62 mA/cm^2, with separate samples being used for each measurement. Since the hydrogen diffusivities are known for only AISI 4340 and AISI 4130 steels, these are the only materials for which hydrogen concentrations can be determined on an absolute basis.

For hydrogen elimination studies, samples of several high strength steels, after determination of the sample blanks, were electrolyzed at the same current density (62 mA/cm^2) for 30 min to establish the initial hydrogen concentration. For a given alloy, samples were then baked at 65.6°C for different lengths of time to eliminate hydrogen, with separate samples again being used for each measurement. Although 190.6°C (375°F) is the temperature usually recommended to eliminate hydrogen, it was necessary to use 65.6°C (150°F) in these studies in order to follow the rate of elimination. Further details of the hydrogen elimination problem will be discussed in the following section.

For the electroplating experiments, type AISI 4340 steel was electroplated completely with both bright Cd and dull Cd electroplating solutions, and then completely stripped of Cd with NH_4NO_3 solution in order to make the electrochemical measurements. Electroplating was accomplished at a current density of 32 mA/cm^2 for a period of 10 min in the bright Cd case and at a current density of 22 mA/cm^2 for 15 min in the dull Cd case.

RESULTS AND DISCUSSION

A. Hydrogen Uptake

The uptake of hydrogen by AISI 4340 steel as a function of time of electrolysis is shown in Figure 4. As expected, the curve is indicative of an asymptotic approach to a saturation value. If the atoms of hydrogen are assumed to lie on the surface of the sample, a total of about 2.0 x 10^{17} atoms would be contained in an area of 1 cm^2 at a hydrogen concentration of 0.35 ppm. Assuming a close packed monomolecular layer of hydrogen, approximately 2.0 x 10^{15} atoms could occupy an area of 1 cm^2. Thus, there are 100 times as many atoms as could be accounted for with a monomolecular layer, and some of the hydrogen must have diffused into the interior of the metal.

B. Hydrogen Elimination

Experimental procedures for determining the rate of hydrogen elimination have been discussed. The elimination of hydrogen appears to follow a first order rate law rather satisfactorily. That is, it obeys the relation

$$\frac{-dC}{dt} = kC \quad . \tag{6}$$

Here, C is the hydrogen concentration at time t, and t is the time of baking at a given temperature 65.6°C (150°F). Equation (6), upon integration and imposition of proper boundary conditions, becomes

$$\ln \frac{C}{C_o} = -kt \quad . \tag{7}$$

Here C is the hydrogen concentration at time t, and C_o is the initial hydrogen concentration, established as described previously. In this case, absolute values of the hydrogen concentration need not be known, since only the ratio C/C_o is involved. This ratio is given simply by equation (3):

$$\frac{C}{C_o} = \frac{I_p}{I_{p_o}} \quad . \tag{8}$$

Thus, it is necessary to know only the ratio of the diffusion current densities, since the diffusion constant D cancels out in taking the ratio. A plot of Ln C/C_o versus time of baking is shown in Figure 5 for Rene' 41 and is seen to follow rather closely the first order dependence.

The rate constants and half-lives for hydrogen elimination are given in Table 1 for several alloys. The half life for hydrogen elimination is given by

$$t_{1/2} = -\frac{1}{k} \ln 0.5 = \frac{0.693}{k} \quad .$$

In general, materials which are susceptible to hydrogen embrittlement display smaller values of the rate constant k and larger values of the half lives for hydrogen elimination. There are exceptions to this trend for type 1010 steel and 316 stainless steel. Although these materials show rather large half lives, they are not known to be susceptible to hydrogen embrittlement. Hence, there are undoubtedly other factors involved in evaluating a tendency toward hydrogen embrittlement.

C. Heat Treating

This experiment was undertaken to determine the effect of heat treatment on hydrogen retention times, which might be reflected in a tendency toward hydrogen embrittlement. Four materials, AM-355 stainless steel, AISI 4130 steel, 410 stainless steel, and 18 Ni (250) maraging steel, were subjected to the heat treatments described in Table 2. Rate constants and half lives for hydrogen elimination for these four materials, both before and after heat treatment, are listed in Table 3. As usual, the samples were charged with hydrogen immediately before initiation of the hydrogen elimination studies. With the exception of 18 Ni (250) maraging steel, where the parameters are identical before and after heat treatment, the effect of heat treating is to increase the retention times for hydrogen. This may possibly be due to a change in structure during the heat treating process.

D. Electroplating

Type AISI 4340 steel was chosen for this experiment both because it is known to have a high tendency toward hydrogen embrittlement and because the diffusion coefficient for hydrogen is known, so that hydrogen concentrations can be determined on an absolute basis. Both bright and dull Cd plating solutions were used because Cd plating is known to cause hydrogen embrittlement, with the dull Cd plating case being more hydrogen embrittling than the bright Cd case. The procedure used in plating and measuring hydrogen concentrations was described previously. The hydrogen concentration obtained for the dull Cd plating was 0.07 ppm, while that for the bright Cd plating was 0.02 ppm. While these values are lower than expected, they nevertheless reflect the greater tendency toward hydrogen embrittlement for the dull Cd case.

CONCLUSIONS

The results of this study indicate that the EG&G-PARC Model 350A corrosion measurement system can be used successfully to determine small hydrogen concentrations. While it would be desirable to verify these measurements with the hydrogen extraction or vacuum fusion techniques, the concentrations of hydrogen are generally too low for accurate measurements using these methods.

The results indicate that hydrogen uptake is not linear with time of electrolysis, but rather asymptotically approaches a saturation level with time. The results also indicate that some of the hydrogen diffuses into the metal. Although exceptions occur, agreement is found generally between hydrogen retention times during hydrogen elimination by baking and the tendency toward hydrogen embrittlement. Also, the effect of heat treating high strength steels is to increase hydrogen retention times. Hydrogen uptake during electroplating, using bright Cd and dull Cd plating solutions, is not as great as expected, although the results of this study indicate that hydrogen uptake in the dull Cd case is greater than that in the bright Cd case. This would be in agreement with the fact that dull Cd plating is more hydrogen embrittling than bright Cd plating.

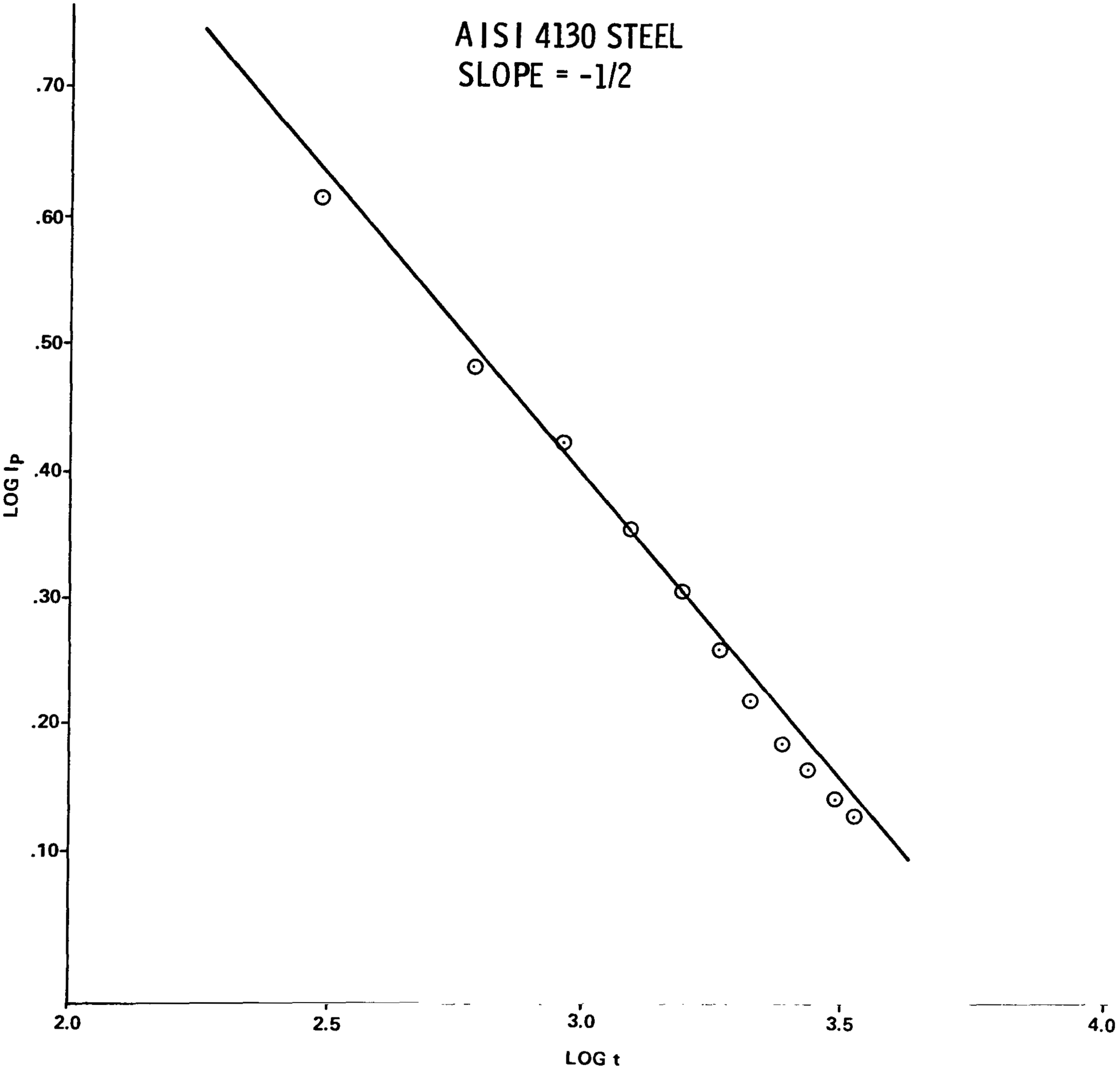

Figure 1. Plot of log I_p versus log t for AISI 4130 steel.

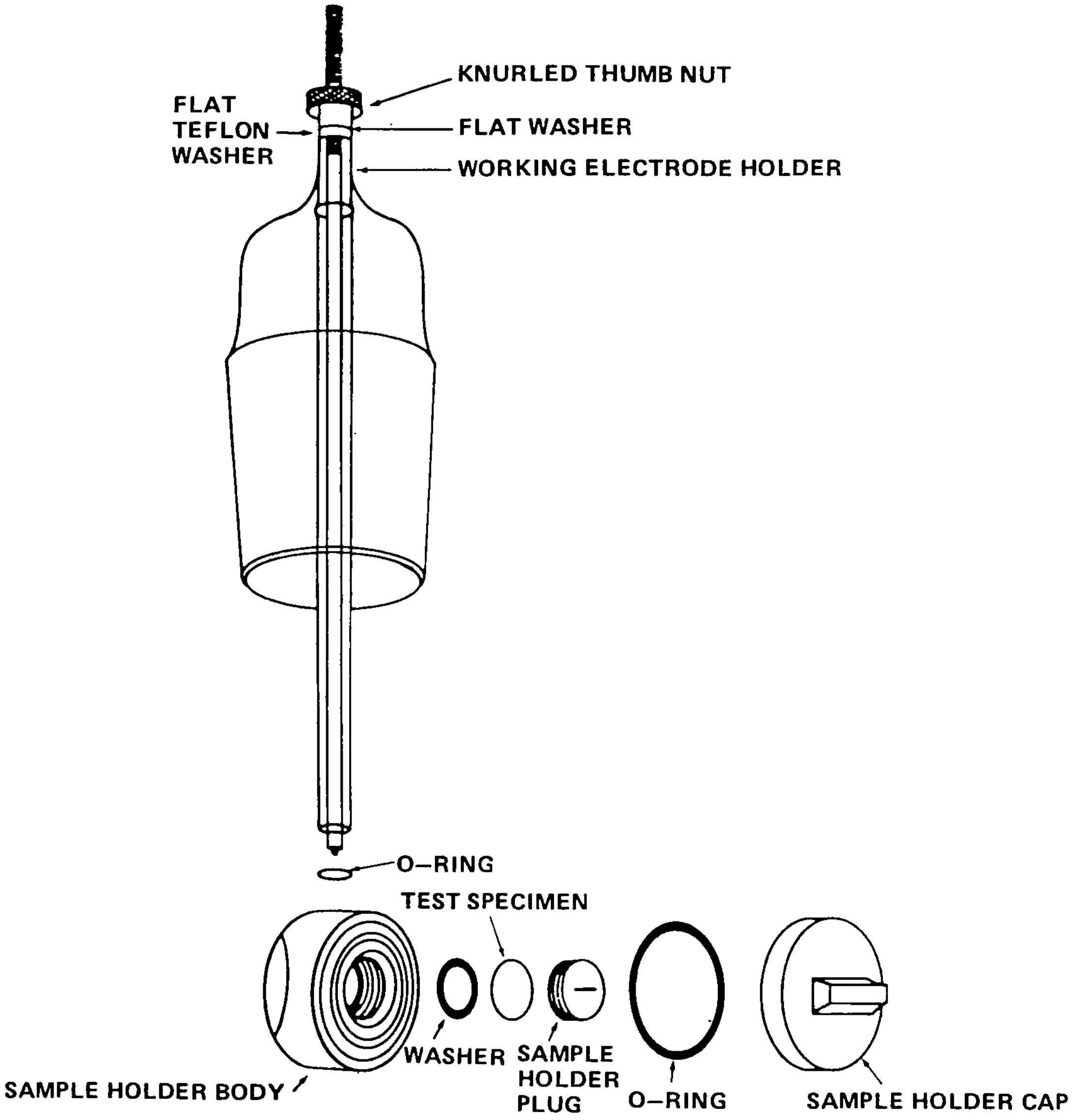

Figure 2. Exploded view of the sample holder.

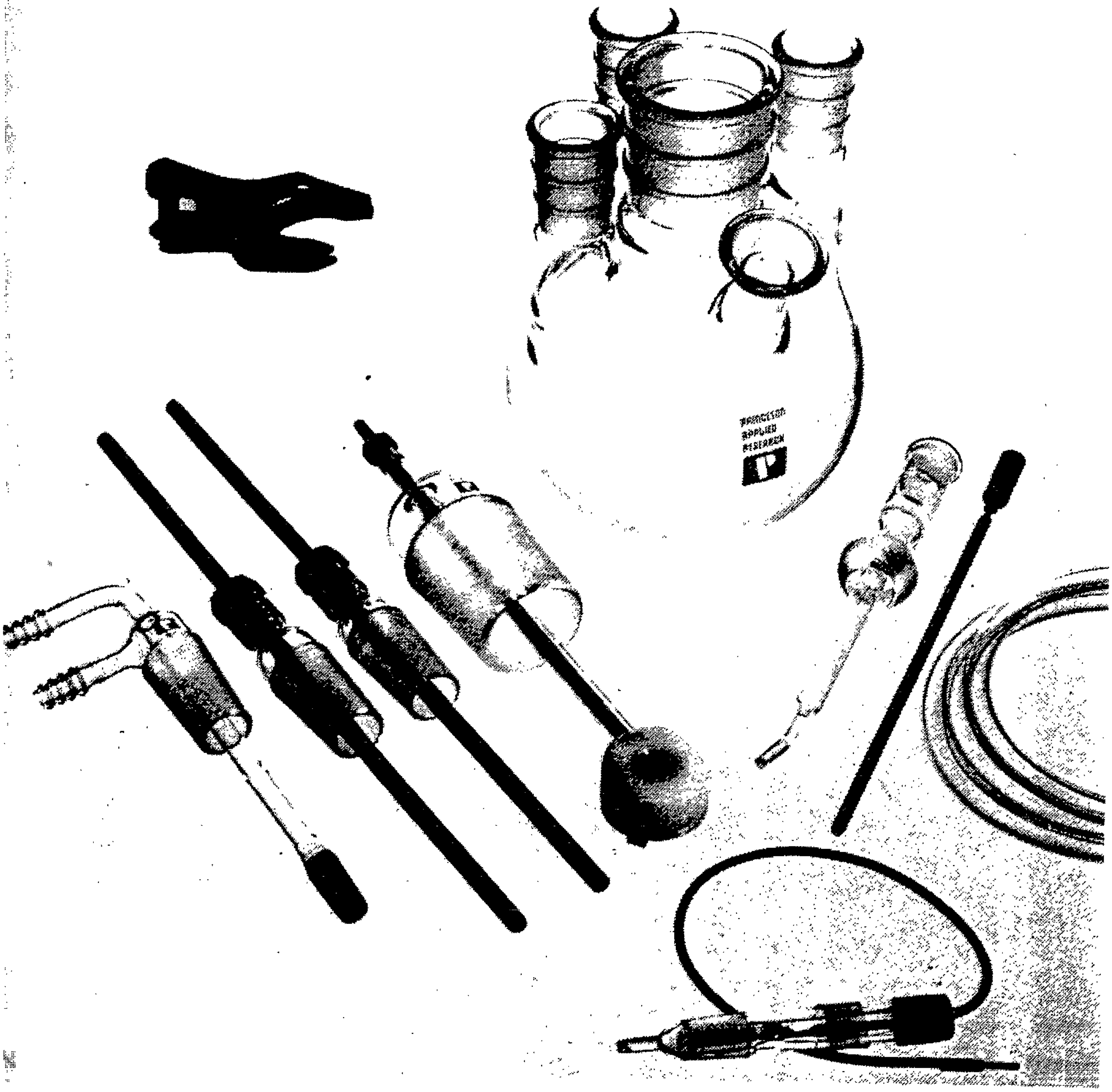

Figure 3. View of the corrosion cell system.

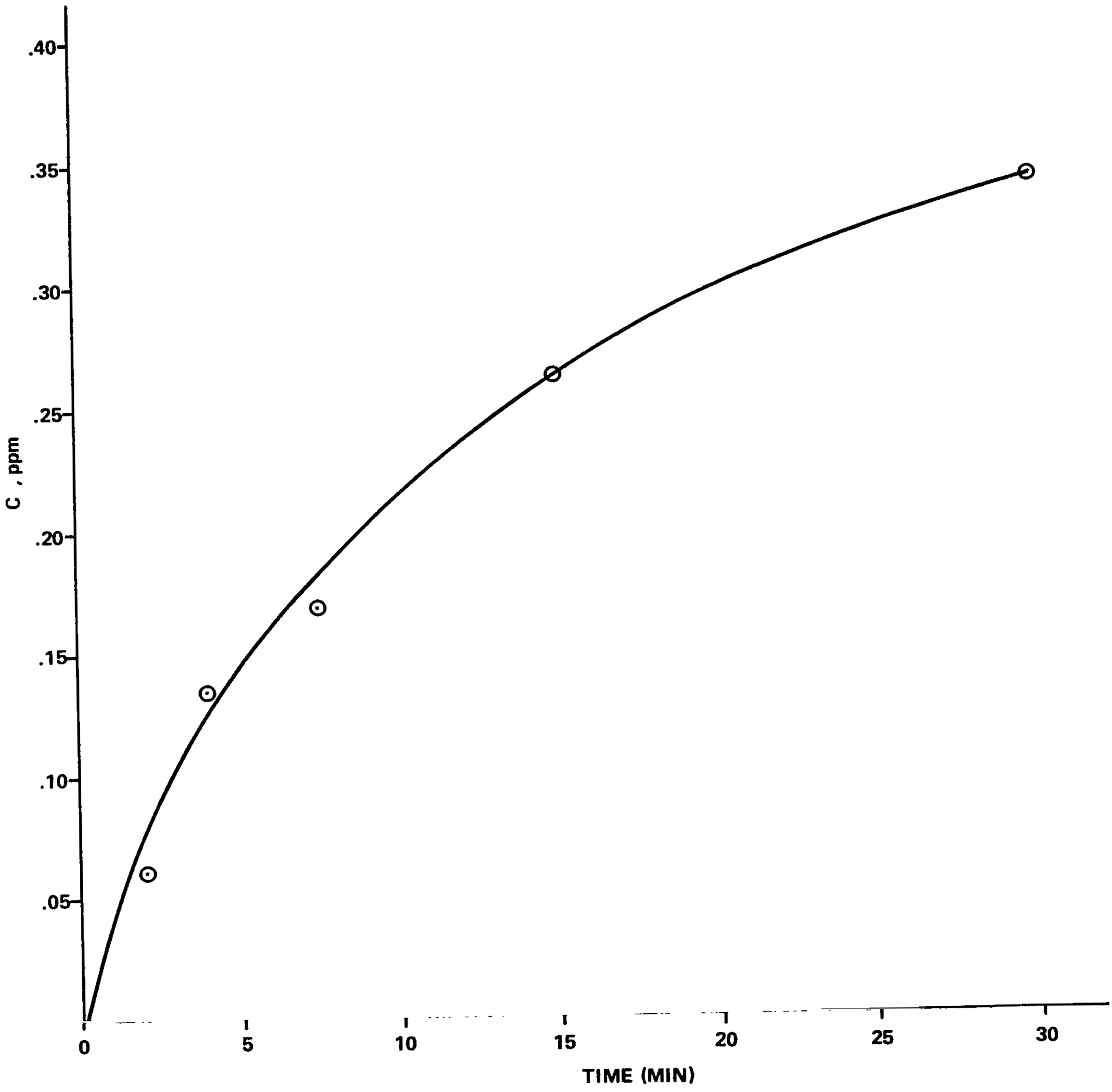

Figure 4. Uptake of hydrogen by AISI 4340 steel during electrolysis.

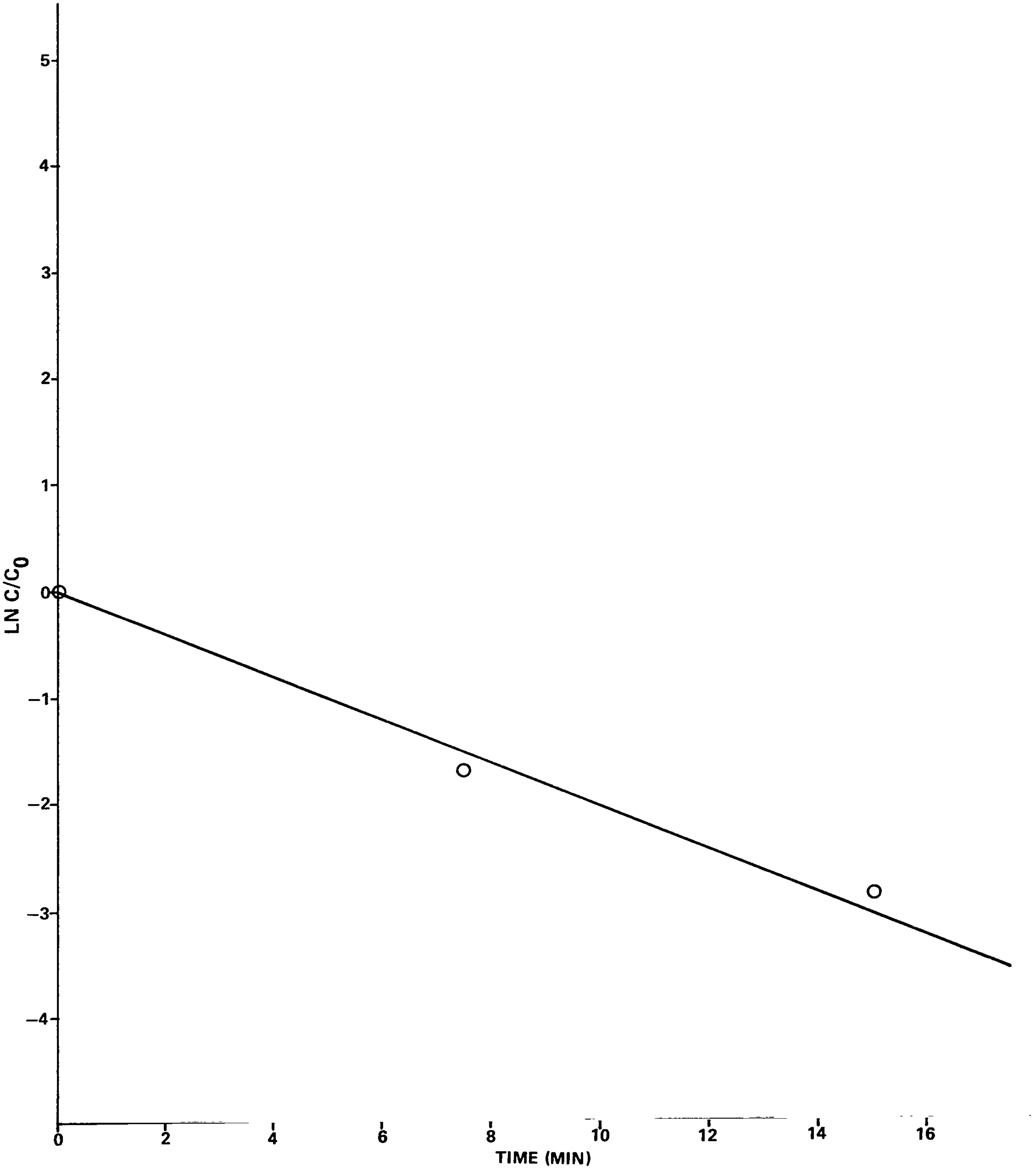

Figure 5. Hydrogen elimination by Rene′ 41 showing first order dependence.

TABLE 1. RATE CONSTANTS AND HALF LIVES FOR HYDROGEN ELIMINATION

Alloy	k(hr^{-1})	Half Life (min)
4340 Steel	2.1	19.8
4130 Steel	2.4	17.3
17-7 PH SS	6.9	6.0
17-4 PH SS	7.0	5.9
410 SS	6.5	6.4
AM-355 SS	8.2	5.1
18 Ni (250) Maraging Steel	10.0	4.2
Inconel 718	9.5	4.4
Rene′ 41	12.3	3.4
1010 Steel	1.1	37.8
430 SS	7.1	5.9
600 SS	9.2	4.5
304 SS	19.9	2.1
A286 SS	13.0	3.2
321 SS	13.1	3.2
316 SS	4.6	9.0
347 SS	13.4	3.1

TABLE 2. HEAT TREATMENTS OF THE ALLOYS INVESTIGATED

Material	
AM-355 Stainless Steel	Austenitize at 1066°C in vacuum furnace for 30 min, water quench, austenitize at 954°C in vacuum furnace for 45 min, water quench, refrigerate at -73°C for 3 hr, age in air furnace at 538°C for 3 hr, air cool.
AISI 4130 Steel	Austenitize at 843°C in argon for 30 min, oil quench, temper at 454°C for 2 hr, air cool.
410 Stainless Steel	Austenitize at 968°C for 45 min, in argon, oil quench remove oil, temper at 302°C for 2 hr, air cool.
18Ni (250) Maraging Steel	Austenitize at 816°C in vacuum furnace, argon cool, harden at 482°C for 3 hr, air cool.

TABLE 3. COMPARISON OF RATE CONSTANTS AND HALF LIVES OF VARIOUS STEELS BEFORE AND AFTER HEAT TREATMENT

	Before Heat Treatment		After Heat Treatment	
Alloy	k_1 (hr^{-1})	$t_{1/2}$ (min)	k_2 (hr^{-1})	$t_{1/2}$ (min)
4130	2.4	17.3	0.23	180.8
410	6.5	6.4	4.6	9.0
AM-355	8.2	5.1	6.6	6.3
18 Ni (250) Maraging Steel	10.0	4.2	10.0	4.2

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16. ABSTRACT

An electrochemical method has been developed for the determination of hydrogen in metals using the EG&G-PARC Model 350A Corrosion Measurement Console. The method has been applied to hydrogen uptake, both during electrolysis and electroplating, and to studies of hydrogen elimination and the effect of heat treatment on elimination times. Results from these studies are presented.

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